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PITMAN METALLURGY SERIES

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FOUNDRY SCIENCE



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FOUNDRY SCIENCE

*FUNDAMENTALS UNDERLYING
FOUNDRY PRACTICE*

by

HARRY A. SCHWARTZ

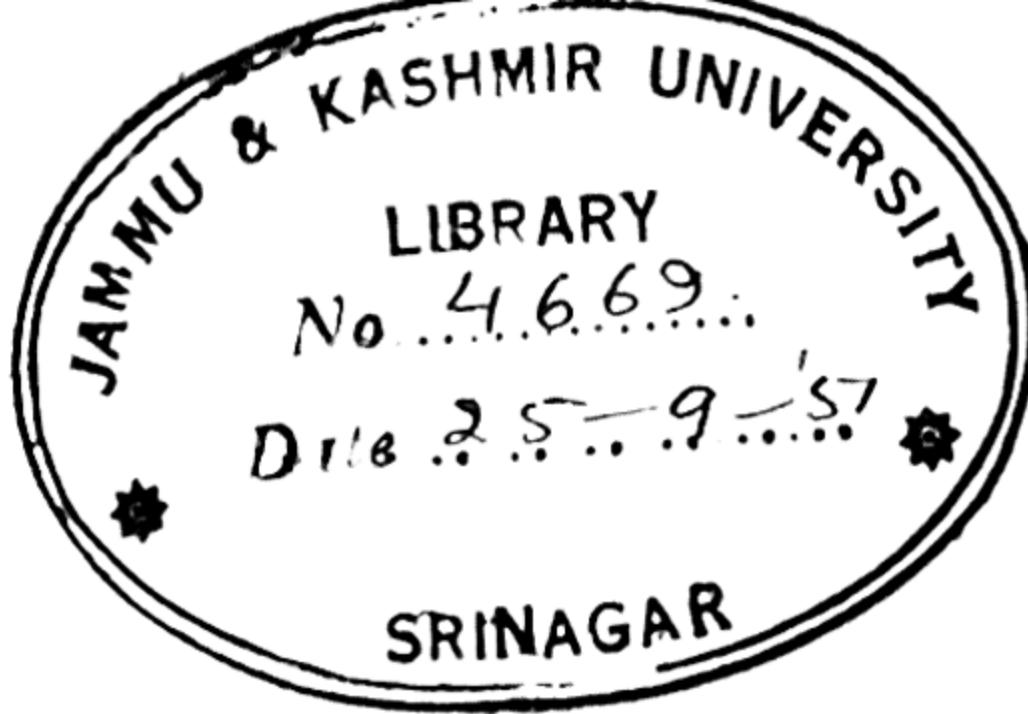
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Preface

THE INSPIRATION FOR THIS text goes back to a statement by Sir W. Lawrence Bragg in the writer's hearing, to the effect that what industry most needed was someone to interpret the findings of the scientist to the industrial technologist. By implication the practical applications should be left to the latter. Hence this is not a scholarly book. Even if the author could have written profoundly, the foundryman would not have read his text. Nor is it a handbook of foundry practice. The author did not wish to describe an art but to deal with the scientific basis of that art, leaving the reader to get his detailed knowledge from the existing enormous literature.

The content of the present book is, in large measure, an abridgment and simplification of lectures on Theoretical Metallurgy and on Foundry Physics given by the author in the graduate school of Case Institute of Technology.

The book is directed to engineering students contemplating specializing in foundry practice. It may serve to correlate their work in the fundamental sciences with the processes they will encounter in practice.

It is also directed to the foundry engineer, who since his graduation from college may have become sufficiently hazy in theoretical knowledge to make a refresher course desirable.

The order of presentation is thought to be logical for the purpose, since it begins with fundamentals of the properties of matter and energy and then takes subjects in their order in the foundry and not in that of scientific development.

While this has sometimes separated the treatment of a given principle into several parts, it has assembled in one place all of the fundamental concepts pertinent to a given operation.

Every effort has been made to simplify the scientific development of the subject and to eliminate mathematics. The chemist and physicist may criticize the treatment as being of the cookbook character, but our principal audience is probably more interested in a statement of scientific laws and relationships than in a demonstration of their truth. Those who wish to pursue the indicated conclusions to their sources are to be commended and are referred to the numerous purely scientific texts that already exist.

Unfortunately it is not possible to present the information contained in this book in so simplified a manner that it can be read by those having no formal preparation at all in chemistry, physics, and mathematics. The reader is supposed to have at least a reading acquaintance with the elements of these disciplines, including the ability to read simple expressions in calculus notation.

It seems to be true that one does not completely understand a subject in the physical sciences until it can be discussed in quantitative terms. Perhaps we do not know all the pertinent numerical values, but the form of relationships cannot be accurately understood except in equations.

So far as his ability and the character of the subject permit, the writer has avoided a formal, rigorous, and pedantic exposition. The harm done by lack of complete precision is perhaps more than balanced by greater readability.

The desire to avoid a stilted form of presentation has necessitated certain practices that the academically minded

may dislike. Practically all the illustrative diagrams are largely schematic in character and do not pretend to high precision. As understandable a figure as might be attainable was desired rather than the utmost accuracy, especially in fields where there is not complete agreement as to facts among different observers. Nor was it thought desirable to document each statement by reference to the literature, in the form of footnotes. Very obviously only a small part of the facts in such a book are original with the author, but the maintenance of a complete reference file, tracing each statement to the initial authority, was not deemed important either for the original lectures or for this publication.

Well-known laws common to many texts are referred to by the names with which they are customarily identified in the literature. In a few cases, when facts or a viewpoint are largely the work of one man, the publication of origin is mentioned in the text. When literal quotations from known copyrighted material are involved, permission to use the material was obtained from the owner of the copyright.

Nomenclature

Since this book deals with a number of scientific and engineering fields, the selection of symbols has presented some difficulties. The various disciplines involved often use the same symbol to designate different things. For example, had we adhered to the well-established Gilbert Lewis terminology for thermodynamics, it would have been necessary to change well-established usage in other branches of knowledge if some duplications of meaning of symbols were to be avoided.

Such adherence to principle was thought to cause more confusion than it avoided. Usually in every field the terminology of writers most familiar to the author was followed, incurring some risk of confusion when the same letter means different things in different contexts and chapters.

To avoid such confusion as far as possible, the meaning of a symbol is usually given in the text as it is used.

Supplementary Reading

For the guidance of those wishing more extended or detailed information, a Supplementary Reading list is appended comprising both standard texts and recent periodical publications. The list includes both semipopular and highly technical treatments. Textbooks of wide application are in general listed under the chapters where their use seemed most useful.

Acknowledgements

The author's thanks are due to Ginn and Company for permission to quote the heat-transfer equations from Ingersoll and Zobel's *Mathematical Theory of Heat Conduction*; to John Wiley and Sons for permission to quote from *Flow of Gases in Furnaces* the statements attributed to Groume-Grjmailo or Yesmann; and to the American Society for Metals for permission to quote his own work on graphitizing rate from *Kinetics of Graphitization in White Cast Iron* and the Laplanche equation from that author's "A New Structural Diagram for Cast Iron," in *Metal Progress*, and for the use of the iron-carbon diagram. The American Foundrymen's Association has similarly given permission for quotations, mainly in the field of heat transfer and solidification of metals.

While not pretending to any considerable attainment as a physical chemist, the author has attempted to combine the experience obtained during eighteen years of foundry operation, followed by twenty-eight years in the study of such operations from a scientific viewpoint, into something of value to foundrymen who want something better than rule of thumb and tradition for their guidance.

HARRY A. SCHWARTZ

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Energy and the Structure of Matter

UNTIL THE FOLLOWERS of the higher physics had their way with us, foundry metallurgists and all other engineers lived contented and satisfied lives in a fairly simple world. Perhaps it only seemed simple from long acquaintance.

Conservation of Matter and Energy

Matter was indestructible and consisted of only a few more than 80 elements, although others were suspected to exist and the properties of the missing ones could be predicted. These elements could not be transmuted one into another, but they combined in many complex ways; however, they always combined in amounts proportional to the atomic weights of the elements. The constants of proportionality were whole numbers representing *valence*, a characteristic of each element.

Energy could exist in several forms but could not be created or destroyed and constantly tended to convert into the form of heat, which in turn tended to so distribute itself as to reduce temperature differences and therefore become unavailable. And that was that.

To be sure, there were some stumbling blocks. A whole new column had to be added to the periodic table when the noble gases, which do not possess valence, were discovered. Some elements had a disconcerting variety of valences; manganese, for example, is unkind enough to form all the oxides from MnO to Mn_2O_7 . The construction of so-called structural formulas was done very successfully by the organic chemists, but assigning an explanation for such a compound as Fe_3C , in which carbon (valence 4) combined with 6 or 9 iron valences, or else iron combined with itself, smacked of puzzle working rather than science. Also some atomic weights, such as that for chlorine (35.457), were certainly not whole numbers within the precision of experiment, and iodine (126.92) and tellurium (127.61) were apparently interchanged in the periodic table, a matter that caused some able men to doubt whether the latter was an element.

Despite all this we got along happily in our ignorance in a world in which all things could be measured when reduced in the last analysis to terms of length, mass, and time.

Relativity

Here the relativists upset the applecart. It had always been thought that radiation was transmitted in a highly mysterious and somewhat improbable substance, called the luminiferous ether, having no mass and enormous rigidity and pervading all space. Michelson and Morley's famous experiment had shown that if there were such a medium the earth did not move through it. The development under the leadership of FitzGerald, Lorentz, and Einstein of the relativity theory that time, length, and mass are not invariable but depend upon the relative velocities of the observer and the observed, knocked our former concept of an orderly universe literally askew.

Minkowski introduced us into a four-dimensional world

in which to the familiar length, breadth, and thickness, time is added as a dimension. If I am to describe my position in the cosmos I must not only say that I am on the third floor of a building at 42nd Street and 5th Avenue, but I must also say at what time I am there. In Minkowski's world a second on the time scale is equivalent to 186,000 miles on the distance scale.

According to present-day relativity ideas the mass of a body increases, and its length decreases as its speed with reference to the spectator increases until, if the body moves with the velocity of light, its mass becomes infinite and its length in the direction of motion becomes zero. Fortunately we do not often measure projectiles flying past us much more rapidly than rifle bullets, but the researcher in modern physics does measure the mass of electrons or helium nuclei that have velocities important in this connection.

Even though we do not deal, in foundries, with velocities comparable to that of light or with particles comparable to atoms or electrons, a few conclusions of the relativists will be of interest in connection with future thinking. Matter is a form of energy. The energy available when matter disappears (it is not destroyed but only converted to an equivalent amount of something else) is represented by the equation

$$E = Mc^2,$$

which says that the energy that appears (in ergs) when a given mass M (in grams) of anything disappears is the product of the mass and the square of the velocity of light (3×10^{10} cm sec⁻¹). Obtaining power directly from the destruction of matter, which perhaps goes on in the stars, has become the contemporary philosopher's stone. Just how enormous this source of power might be can be realized by comparing the amount of energy evolved by burning 1 gram of carbon to CO₂ (7859 cal) with the amount equiva-

lent to its complete conversion into energy (21.5×10^{12} cal), a ratio of 2,700,000,000 to 1.

It also appears that certain very fundamental concepts, with which we shall deal later, do not change in magnitude because of relativity considerations. These are number, entropy, and action, that is, the product of energy and time. Also the world of relativity is so constructed that the velocity of light is always the same.

Atomic Structure

The atomic physicists were interested in explaining the familiar periodic table of Lothar Meyer and Mendelejeff. The latter thought of his table mainly as an empirical record of observed fact. The later students substituted for the idea of a series of elements, which had grown to 92 in number, the idea of more fundamental building blocks, protons and electrons. We may note in passing that later they had to add other units, the neutron, the positron, the neutrino, and the mesotron, with which we need not have much to do.

Protons and electrons have mass and electrical charge, which is about all one can say as to their characteristics. Their electrical charge is 4.80×10^{-10} static cgs unit of charge, or 1.60×10^{-19} coulomb. The charge on the electron is negative; that on the proton positive. The proton weighs 1.66×10^{-24} g; that is, there are about 6 followed by 23 zeros protons in a gram. The electron weighs about 1/1800 of this amount, or 9.1×10^{-28} g. Usually one encounters the charge of the electron and the mass of the electron or proton as convenient units of measurement in atomic structure, making unnecessary the awkward conversion to cgs units. It is well, however, to have their values of record.

Out of these units we are to build the existing atoms in some manner that will explain the vagaries of the periodic table as well as its consistencies.

We speak of single atoms, not of aggregates. The hydrogen atom consists of a single proton and a single electron.

A nucleus cannot contain more than one proton and be stable, since the two positive charges would repel one another. For more protons there must be added also neutrons. Nature has a great preference for atoms containing the same number of neutrons as protons. Harkins found that about 85% of the atoms in the earth had this relation. The next choice is one neutron more than the number of protons, which accounts for some 13% of the total.

There are other principles. Atoms containing an even number of neutrons are much more common than those containing an odd number. Similarly, there is a preference for even numbers of protons. The combination of an odd number of both neutrons and protons is almost unknown.

The number of neutrons in excess of the number of protons increases with the atomic number (number of protons), and the range in atomic numbers capable of retaining a given excess number of neutrons decreases with the atomic number. Atoms of low atomic number exist in much larger quantity in the universe than the heavier ones.

Each atom contains a number of electrons equal to the number of protons arranged outside the very small central nucleus. What is now called a neutron was at one time thought to be a proton plus an electron, embedded as it were in the assembly of protons. To the foundry metallurgist it will make little difference whether a neutron contains both a positive and a negative charge, which cancel in effect, or whether it contains no charge at all. The neutron is smaller than the electron; hence it cannot contain an electron, as such. It weighs more than a proton plus an electron.

How the electrons are disposed, if not in the nucleus,

has become less and less understandable. J. J. Thomson and Langmuir thought of static patterns; Bohr thought of a series of planetary orbits. According to De Broglie, Heisenberg, Schrödinger, and Dirac the problem can be described only by certain mathematical equations; these would have meaning only to those especially educated in the field.

This much remains of use to the chemist. As electrons and protons are added the former arrange themselves in layers. Hydrogen and helium have one layer containing one or two electrons. Then another layer is started that may contain from 1 (lithium) to 8 (argon) electrons. Then another layer is started and so on.

The outer layer or shell, most important to us, can never contain over 8 electrons, and elements having the same number of outer (or valence) electrons have similar chemical and related properties.

It is not always true that inner shells of electrons are completely filled before the outer shell is begun. It is possible, then, to have elements, such as the transition triads and the rare earths, that have the same number of valence electrons but a different number of electrons in the inner shells, and, because of the corresponding difference in the number of protons, different atomic weights, accounting for a similarity of chemical properties, such as valence, for atoms of successive atomic numbers.

Also many elements are known to be mixtures of *isotopes*, that is, they have nuclei of different masses but identical outer electron shells. Their constancy of atomic weight, as in chlorine, is due to the fact that they are mixtures in nearly constant proportions of two or more isotopes. Any given atom is, of course, of one isotope only.

The distribution of electrons into energy levels and the existence of isotopes in natural elements satisfactorily account for the periodic table. The metallurgist will find use mainly for the knowledge that the outer shell of elec-

trons, containing from one to eight electrons, chiefly account for the manner in which one element differs from another, differences of atomic weight being of less importance.

This may be a suitable place to bring into the picture some of the relations developed by Hume-Rothery and others between atoms and their configuration into crystal lattices.

Atomic Arrangement

We shall later have frequent occasion to speak of *solid solutions*. Crystallographically, these are, very generally, the lattice of the solvent metal in which certain atoms are replaced by those of the solute, usually with some slight distortion. In order that solid solubility may exist at all, the atoms cannot be too different in size, which here means their distance of closest approach in the pure metal's lattice. If atoms differ by more than 15%, solid solubility is very limited indeed.

The formation of interstitial solutions by inserting a very small atom (H, C, B, and the like) into a vacant space between the atoms in a lattice is here disregarded.

Plainly, if there is to be complete solubility of one element in another in the solid state, the two must have the same lattice type or at some concentration the type will change and there will not be a continuous series of solutions. By lattice type is meant the pattern the atoms make in space, face-centered cubic, body-centered cubic, and so on.

If the atoms are in widely separated columns of the periodic table, the tendency to form compounds, that is, new substances of perhaps greatly differing lattices, will overbalance the tendency to substitute for other atoms, and little or no solubility will exist.

The average number of valence electrons per atom in intermetallic alloys is related to the lattice type, according to Hume-Rothery. For example, in body-centered cubic

lattices this number is likely to be near $3/2$, and other relations exist for other types. The agreement is by no means perfect, however. Fractional numbers of valence electrons per atom cannot, of course, exist in elements, but are limited to intermetallic solutions or compounds.

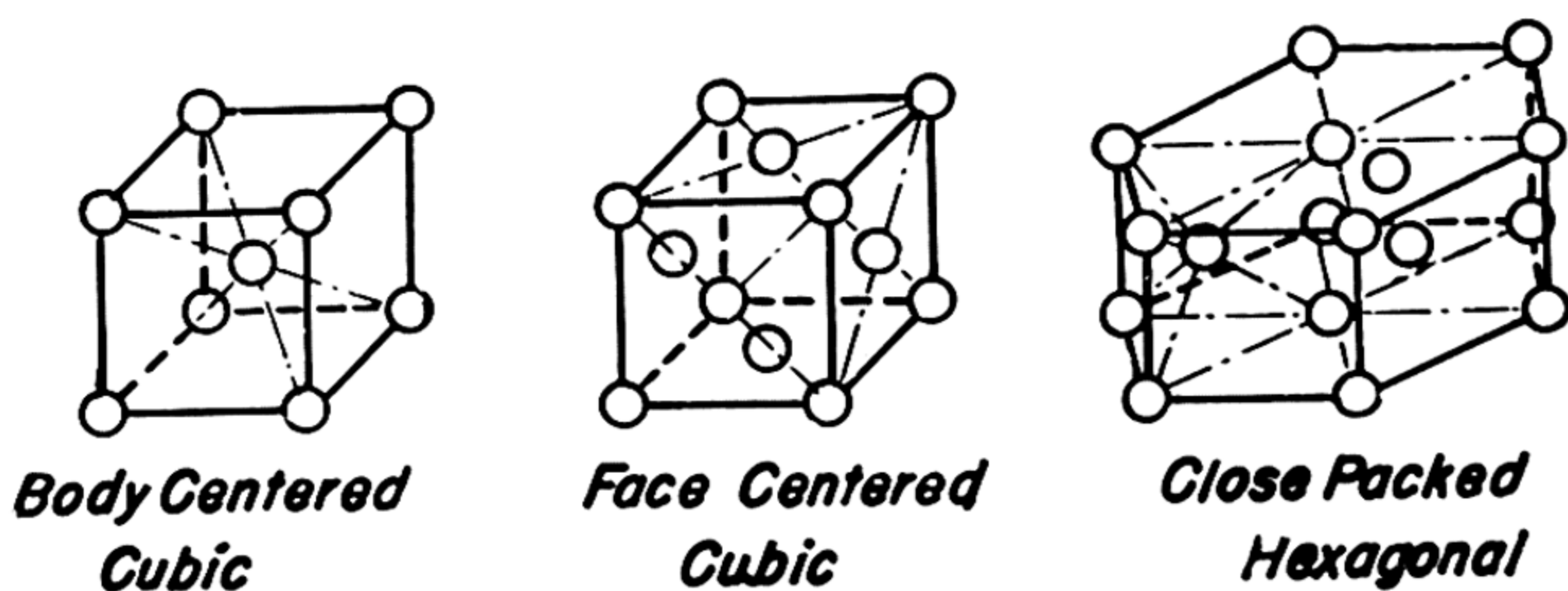


FIG. 1-1. Common Metal Lattices.

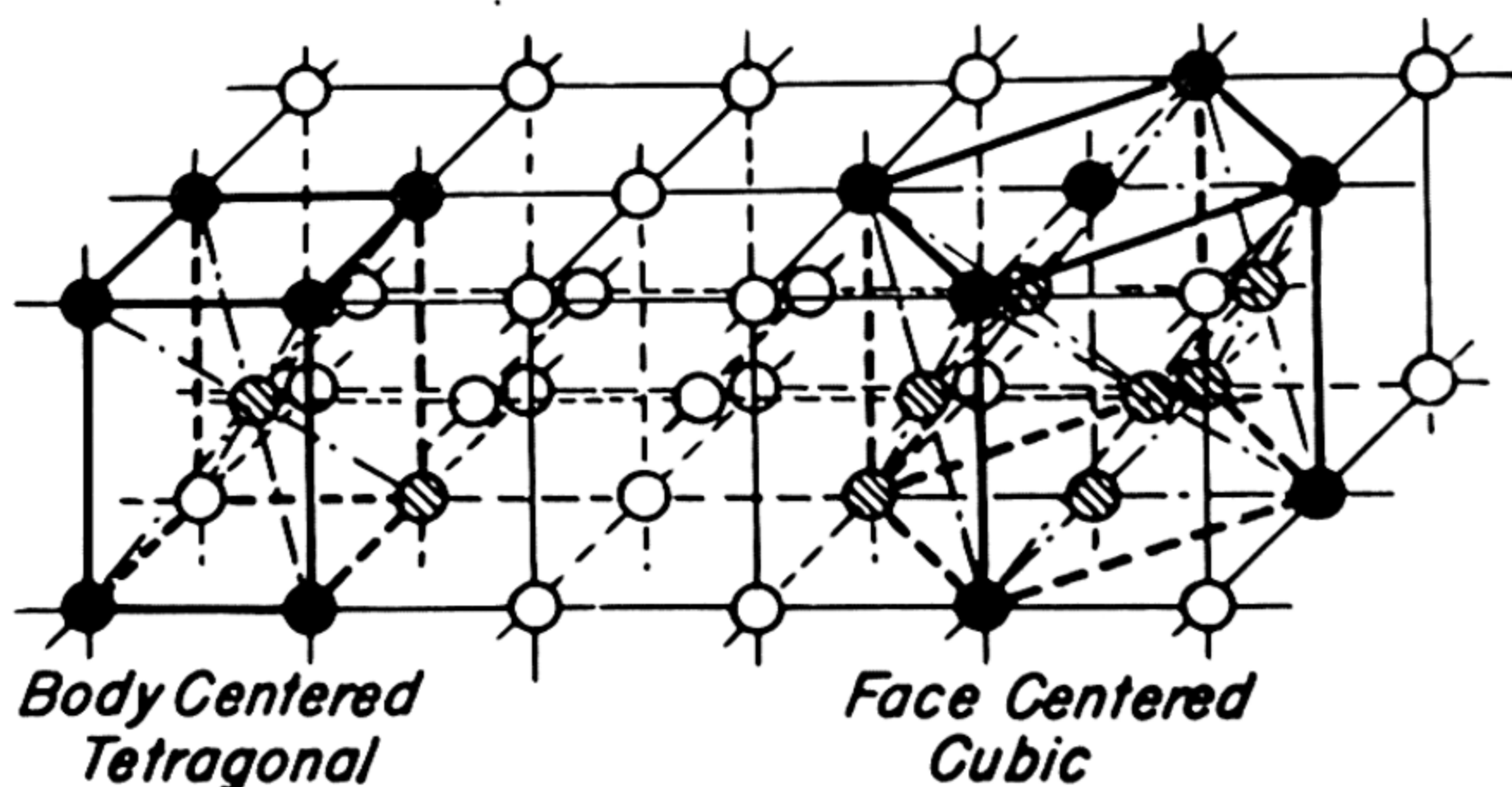


FIG. 1-2. Relation of Lattice Nomenclature to Axes of Reference.

The atomic physicists are able to assign reasons for these lattices, based on the possible energy levels of electrons in a crystal. These are beyond the understanding of those not versed in their methods.

Many of the important elements have their atoms arranged in body-centered cubic lattices; such are chromium (alpha) iron, magnesium, molybdenum, and vanadium. Many others are face-centered cubic, such as aluminum, copper, gold (gamma) iron, and silver. Silicon and zinc,

for example, are hexagonal close-packed. These lattices are illustrated in Fig. 1-1. The type of lattice depends somewhat upon the axes of reference chosen by the observer. Fig. 1-2 shows that a given array of atoms in space might be considered either body-centered tetragonal or face-centered cubic.

Structure of Fluids and the Phase Rule

MOLECULES HAVE NOT been so interesting to the X-ray diffractionists, who prefer to talk about crystal lattices. Still, we cannot ignore them. The best proof of their existence in gases is the reasoning that led to Avogadro's law that equal volumes of gases at a given temperature and pressure contain equal numbers of molecules (not atoms). The statement, like so many early laws, is only approximately correct. It is exact for *ideal* gases, of which more shortly.

Gram Molecules

Much more recently, the number of molecules in a gram equivalent of any substance has been determined. It is 6.06×10^{23} and is called Avogadro's number or the Loschmidt number.

This number is useful as well as interesting, for it makes it possible to calculate quickly the density of any gas, using the principle that the densities of gases under given condi-

tions are proportional to their molecular weights. Conversely, we may compute molecular weights from densities.

Equation of State of a Gas

Ideal gases have as an equation of state correlating their pressure, temperature, and volume the expression

$$pV = RT. \quad (1)$$

Here p is pressure, V the volume of a gram molecule, T the absolute temperature, and R a universal constant called the gas constant. Its numerical value depends upon the units chosen for p , V , and T . If p is in atmospheres, V in liters, and T in Kelvin degrees (absolute Centigrade scale), R is 0.08205. The liter atmosphere is rather a queer energy unit; if we use the more common energy unit, the calorie, R comes out 1.987. (1 cal = 0.04132 liter atmosphere.)

In ideal gases the molecules are supposed to be so far apart that they do not exert any forces on each other, and that their own total volume is negligible compared with the entire volume occupied by them in their random flight. Any gas can be made ideal if its density be reduced enough by a decrease in pressure or by an increase in temperature. This statement is true, provided heat does not dissociate the molecule (as it does the triatomic molecule of iodine vapor, or the 4-atom molecule of NH_3 , for example). A more general equation of state is van der Waals'

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT. \quad (2)$$

In this equation the term b is intended to correct for the fact that molecules have volume, and a/V^2 for their mutual attraction. If a and b are zero—that is, if the volume and attraction forces are too small to consider—we have an ideal gas, and Equation (2) reduces to Equation (1), the equation of state of a perfect gas.

If one were to plot (as in Fig. 2-1) pressure against

(molar) volume for a sufficiently low value of T in Equation (2), a curve would be found showing three values of V for a given value of p . The lowest volume of the three is the volume of a mole of the liquid compound, the highest that of the gas; the intermediate molar volume, if one exists, corresponds to a purely imaginary state in which the fluid cannot exist in nature, so we may as well forget about it.

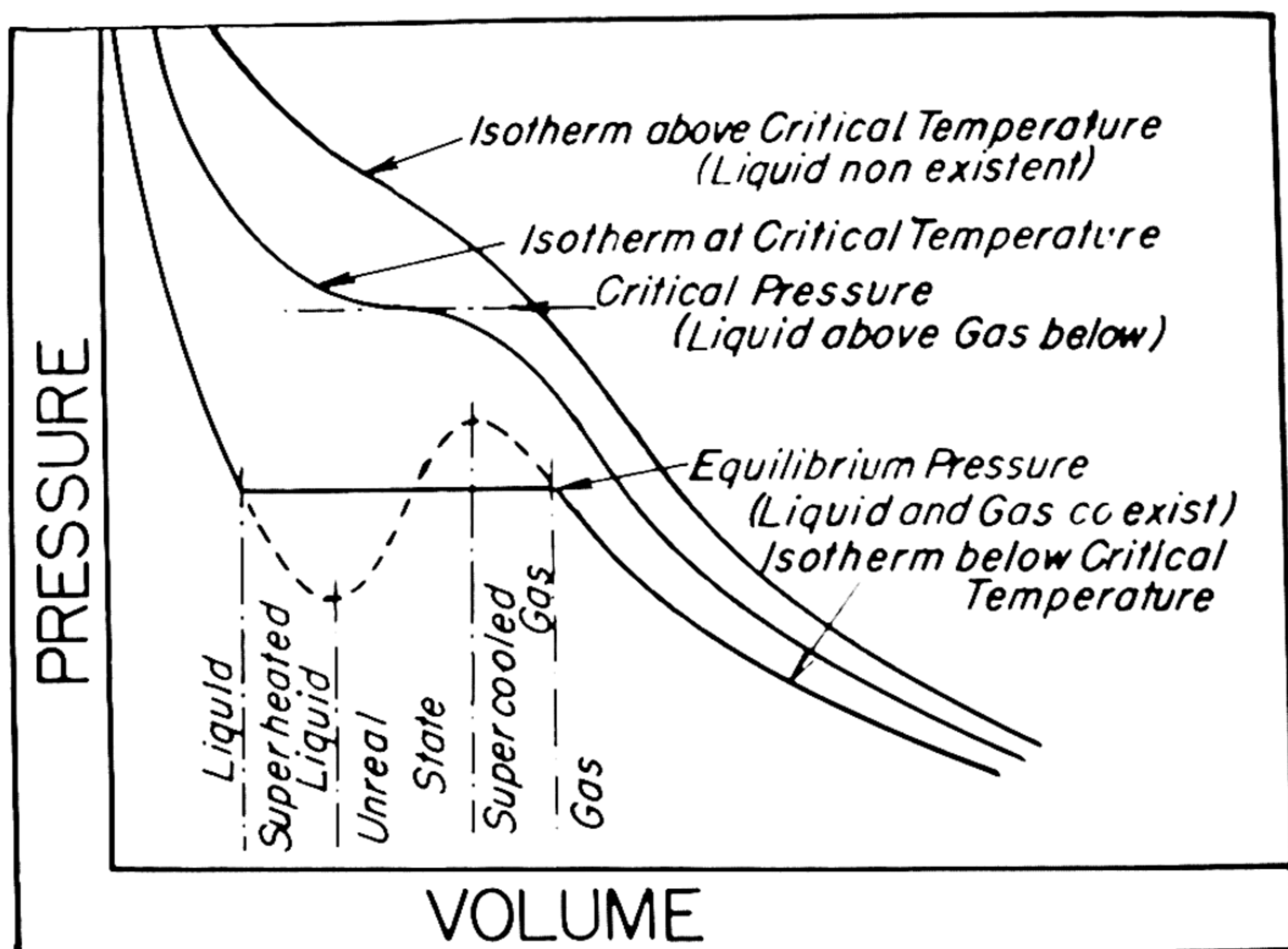


FIG. 2-1. Pressure-Volume Relations of van der Waals' Equation.

Now, how big is the molar volume? that is, what is the volume of a mole or gram molecule of our ideal gas? It must be the same for all gases, for the number of molecules in a given volume is the same, and the mass of a given volume is therefore proportional to the molecular weight.

A liter of H_2 (molecular weight 2) weighs 0.08988 g at 1 atmosphere pressure and $0^\circ C$ ($273^\circ K$). The volume of a gram molecule is then $2 \div 0.08988$ or 22.252 liters. We can then calculate, for any gas that is approximately ideal,

the density under standard conditions, if we know the molecular weight, by dividing the latter by 22.252 (or multiplying by 0.04494). This calculation has practical utility.

Also we can in principle construct a temperature scale by observing the pressure in atmospheres at which the volume of a gram molecule of a gas is 22.252 and modifying Equation (1) to read:

$$\begin{aligned} T &= \frac{pV}{R} \\ &= \frac{V}{0.08205} p \\ &= \frac{22.252}{0.08205} p \\ &= (271+)p. \end{aligned}$$

The correct coefficient would be 273+. The difference resides in just what gas is selected, since none is quite ideal. The density of helium would have given 272.95, or very nearly the accepted value.

We have now come to the consideration of liquids and gases, which can be lumped together as fluids. The principal reason for talking about van der Waals' equation has really been to introduce the study of the change of any substance from the liquid to the gaseous state.

Critical Temperature

Going back to the graphs that represent this equation, if higher and higher temperatures are chosen, the three volumes for a given pressure become more nearly alike and there is one temperature, called the *critical temperature*, at which all three are alike. Going to still greater temperatures, the locus approaches in form the hyperbola characteristic of Equation (1).

Above the critical temperature there is only one value of V for a given p . In mathematical terms the cubic equation has only one real root and two imaginary ones.

At such higher temperatures the gas cannot be liquefied and the substance remains a gas, no matter what the pressure. This is of practical importance in the liquefaction of gases and in refrigeration.

The reader will ask what molar volume should be chosen to apply to the substance at temperatures where there are three molar volumes, two realizable, for a given pressure. This depends upon the relation of the boiling point to pressure. One may calculate, by methods to which we shall come in time, the substance's boiling point at the pressure in which we are interested. A comparison of this temperature with the isothermal temperature will show whether we have a gas, above the boiling point, or a liquid below it. There will be one pressure, and only one, at which the isothermal temperature is the boiling point. At that pressure the gas and liquid can both exist. At lower pressures the gas exists and at higher pressures the liquid.

Gibbs's Phase Rule

How can one make so positive a statement? It is not just a matter of memory. Gibbs's phase rule, one of the superlatively great scientific generalizations, says that, at equilibrium,

$$C + 2 = P + F.$$

The letter C indicates the number of components in the system, P the number of phases, and F the number of degrees of freedom. A *component*, as the name indicates, is one of the things that make up the system. If we consider boiling, freezing, or solution involving water, the processes being such that water does not break up into its elements or combine chemically, water is a component. Otherwise, say for example its formation by combustion, its elements might have to be considered. A *phase* may be made of one or more components but is uniform throughout, as ice, water, or salt water. The *degrees of freedom* of a

system are the things to which arbitrary value can be assigned and still make a system in equilibrium.

In our present case there is one component, and we have considered the existence of a solid and a liquid phase. Then, $1 + 2 = 2 + F$, or $F = 1$. Having set a temperature and required that two phases shall be in equilibrium, we cannot arbitrarily set a pressure, but must take what comes. On the other hand, if we insist on setting an arbitrary temperature and pressure, then $1 + 2 = P + 2$, and we can expect only a single phase, liquid or gas as circumstances require. The phase rule comes up in many connections. It is introduced here, out of any regular order, partly to emphasize that theoretical metallurgy is one coherent body of facts.

Calculation of Critical Temperature

Let us go back to the very interesting matter of critical temperature, the boundary above which the liquid cannot exist. It is quite easy to calculate this temperature from

$$T_c = \frac{8}{27R} \frac{a}{b}. \quad (3)$$

Here T_c is the critical temperature, and a and b are these coefficients in Equation (2). The calculation requires differentiation of Equation (2), considering T constant and equating the two expressions for which dp/dV is zero. This is equivalent to making the maximum and minimum coincide.

On this critical-temperature graph, there is a point, corresponding to the three equal roots of Equation (2), where dp/dV is zero. The corresponding pressure and volume, called *critical pressure* and *critical volume*, p_c and V_c , are given by

$$p_c = \frac{1}{27} \frac{a}{b^2}, \quad (4)$$

and

$$V_c = 3b. \quad (5)$$

One may evaluate a and b by determining any two of the critical constants or by the method of least squares from a series of observations of V , p , and T .

Van der Waals' equation is not an exact statement of fact, and much discussion of departures and of the relation of a and b to molecular volume and intermolecular forces can be found in the recent literature.

Supercooled Liquids

Van der Waals' methods set no limit on how low an isothermal temperature might be chosen. Unless the substances crystallize, the isotherms might be thought of as reaching temperatures where viscosity has become so high that the substance has become rigid, hence apparently solid without ever passing through a freezing point. This actually happens in glass and in slags, mainly acid, that are vitreous or glassy.

Structure of the Solid State

GASES AND LIQUIDS have been considered assemblages of molecules held together by van der Waals' forces, whatever they may be, in the nature of attraction of masses for each other. The existence of molecules in liquids is also confirmed by certain quantitative relations between their freezing or boiling points and compositions in the case of solutions. Presumably the apparently solid supercooled liquids still contain molecules, or some discontinuity of properties would have been recognized as the liquid cooled.

Crystals versus Molecules

Perhaps we shall not be too much criticized if we regard only crystalline substances as being truly solids. It is characteristic of crystals of pure substances that their atoms are arranged in certain very definite patterns in space. For the metals these patterns are often, though not always, quite simple. In such cases, from the crystallographer's angle, no atom is any more or less associated with its neighbors than another. This and certain specific heat relations have usually been held reason enough for not thinking of molecules in crystalline metals.

Conductivity Electrons

The reason why the elements of the first two columns of the periodic table and the transition metals like to arrange their atoms permanently into definite and usually simple patterns seems to be beyond the comprehension of those not trained in the special fields of mathematics and physics involved. It does not tell much to make the correct statement that this arrangement gives the state of lowest *free energy* for the protons and electrons. That defines any equilibrium. We shall have much to say about free energy later.

An interesting part of the concept of the metallic state is that it implies that when atoms approach as closely as they do in crystals, energy levels lose their distinction and some electrons become no longer a part of a specific atom but of a crystallite. These free electrons account for the property of metallic conduction. Under the influence of a source of current, electrons pass through the metal and out at one end while being continuously replaced at the other.

Conditions are particularly favorable for the existence of these free electrons in elements of the first periodic group, especially the alkalis, and these have very high conductivities.

The location of the outer energy level is unusually far from the nucleus of alkalic atoms, accounting for the low density and high conductivity of these metals.

Interrelation of Physical Properties

It was natural to attempt to deduce, from the theories of the metallic state, data as to the properties of individual metals or to use these theories to explain empirical knowledge. Thus Grüneisen found that the electrical conductivity of simple metals over a wide temperature range could be expressed by

$$\frac{1}{\sigma} = AT^5 \int_0^{\theta/T} \frac{\lambda^5 d\lambda}{(e^\lambda - 1)(1 - e^{-\lambda})}. \quad (1)$$

Here σ is electrical conductivity, A and θ are constants appropriate to each metal, T is the Kelvin temperature, λ is a variable of integration, and e is the base of the natural system of logarithms. The equation was deduced on the assumption that electrical resistance is due to the fact that conductivity electrons are stopped by a given number of collisions, and hence depends on the mean free path these free electrons can travel before striking anything. The relation of this mean free path to the electronic pattern of a metal determines the constants A and θ .

At very low temperatures $1/\sigma$ approaches $124.4AT^5$, at high temperatures $AT/4$. Like all theories based on this new science, that of metallic conduction is not completely accepted in all its details by all experts. The layman can only sit at their feet and gather such thoughts as will help him to useful knowledge. Often approximations unsatisfactory to the theorist suffice the practitioner, and occasionally the reverse is true.

There is also a relation between conductivity for electricity and for heat called the Wiedemann-Franz law, justified by experience and theory, which says

$$\frac{\kappa}{\sigma} = 3 \frac{R^2}{e^2} T \frac{1}{N^2}, \quad (2)$$

where κ is the thermal conductivity, σ the electrical conductivity, R the well-known gas constant, e the charge on the electron, N Avogadro's number, and T the Kelvin temperature. In the ordinary physical units the ratio of the heat conductivity (calories per second at unit temperature gradient) to that of electrical conductivity in reciprocal ohms should be $5.85 \times 10^{-9}T$, a result often closely approached by experiment. See also Equation (2) of Chapter 13.

Grüneisen also found that for a given substance the specific heat has a constant relation to the coefficient of thermal expansion at all temperatures. This means that a

given input of heat expands a given solid metal by a particular amount, no matter at what temperature the heat units are put in.

Structure of Compounds

To learn in this chapter something of the solid metallic state, it is not necessary to consider anything but the elements. Solid solutions are very important to the foundryman but can best be studied after the ground has been cleared by learning a few general principles.

The opposite extreme to metals among crystallized solids are the ionic compounds. These involve usually an element in the lithium or beryllium group (valence 1 or 2) and an element from the oxygen or fluorine group at the opposite side of the table. The principle on which these compounds are formed is that a first-column element, say sodium, has but 1 valence electron in its outer shell, while chlorine, for instance, has 7. Each would like to have an outer shell of 8 and gets this by removing the single electron from sodium, leaving a positively charged *ion*, and adding it to the outer shell of chlorine, leaving it a negatively charged ion. Ions resemble the atoms of the same element, with the addition or removal of electrons.

The two ions of opposite electrical charges now attract each other as any charged particles would. In space, the atoms of sodium chloride occupy the points of a set of cubic cells, these points being occupied alternately by metal and halide ions. There is evidence, based on the distance of closest approach, that the elements are still ionized. They are closer together, center to center, than would be predicted from the shortest distance between atoms in the lattice of the elements. There is no X-ray diffraction evidence that any particular metallic atom is in any way uniquely connected with any one of its neighbors rather than another.

When substances of this kind melt or boil, the liquid or

gas often consists of molecules of the substance, not of atoms of the elements, which shows the bond between two atoms (who knows which two?) to be stronger than that between molecules. A parallel case among the metals is that lithium vapor is diatomic, although there is no uniqueness of relation between any pair of atoms in the solid.

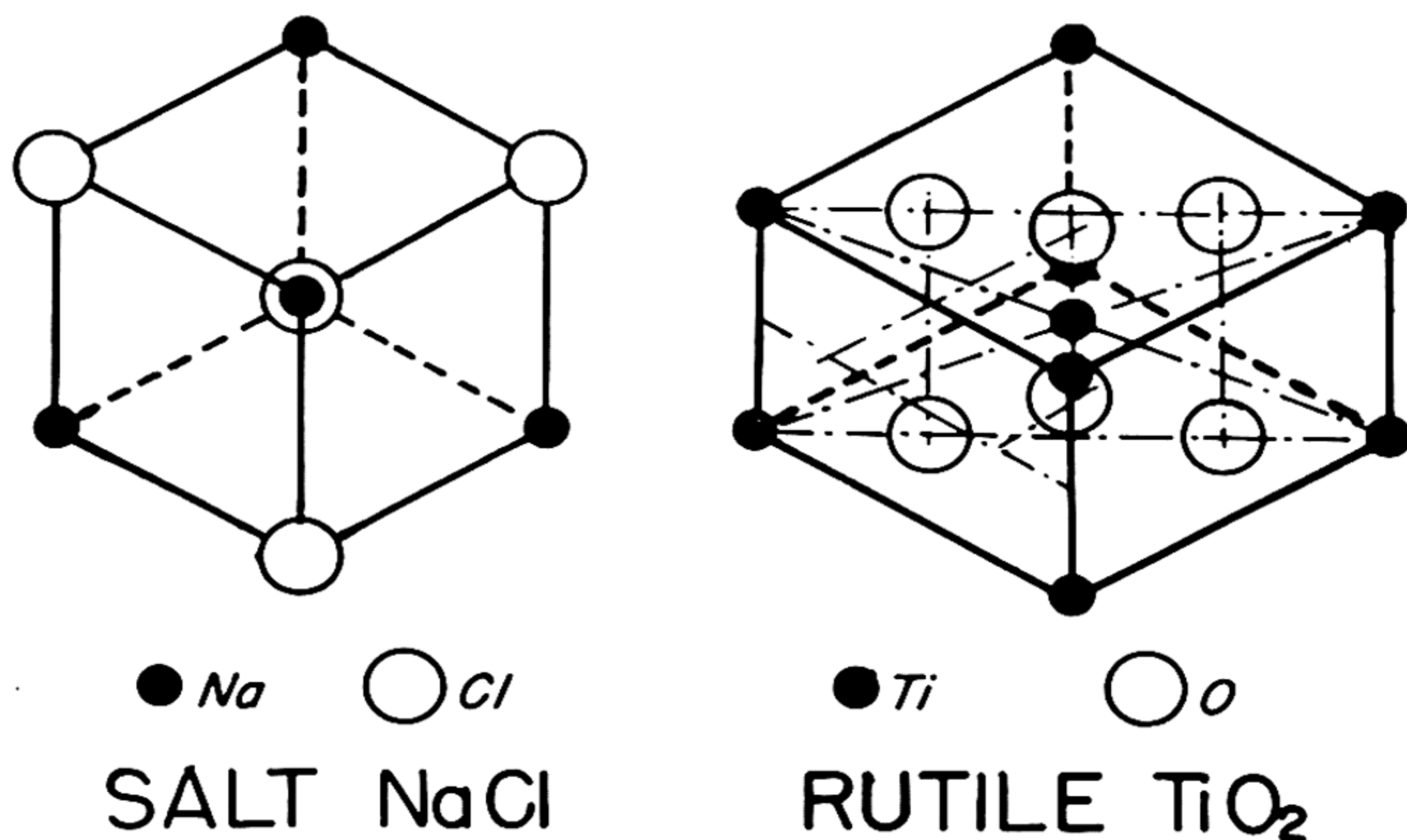


FIG. 3-1. Atomic Arrangement in Polar Compounds. (Based on Wykoff.)

Also, when dissolved in water, ionic compounds behave like molecules partly ionized. Such ionic solutions conduct, not by the transfer of electrons as the metals do, but by the migration of electrically charged matter, ions. The foundryman encounters electrolytic or ionic conduction most evidently in electroplating, although some slag reactions also seem to point to the possibility of ionization.

It is easy to talk too much of space lattices, but it should be said here that some ionic lattices contain units of elements that seem equivalent to single elements. Rutile (TiO₂) is a body-centered arrangement of the TiO₂ group, the Ti atom taking the body-centered positions.

Another type of compound seems to be held together by

forces that tend to surround an atom of a given kind by those of another element arranged in a preferred pattern around the former. These are the so-called co-ordination compounds, of which cementite is an important example. The complex arrangement of atoms in such compounds is shown in Fig. 3-2.

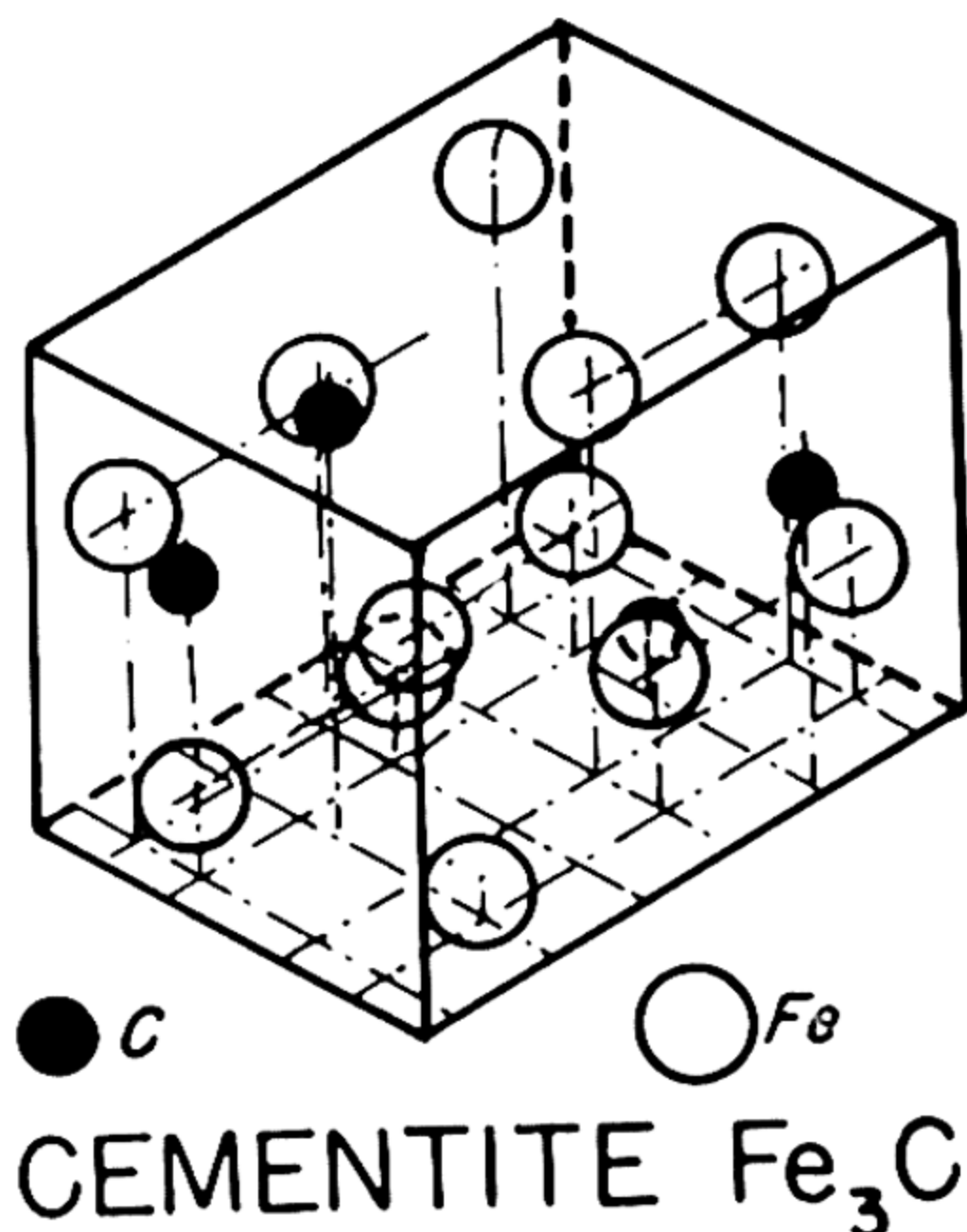


FIG. 3-2. Atomic Arrangement in a Co-ordination Compound.
(Based on Wykoff.)

Lastly there are so-called valence crystals occurring principally among the elements in the middle of the periodic table. Usually these are insulators, the structure permitting of neither electronic nor ionic conduction. Often also they are hard, diamond being typical. They shade off into nonconducting and softer forms similar to ionic crystals. In the case of diamond and some other crystals having similar lattices, each carbon atom is surrounded by four others at the corners of a regular tetrahedron, that is, a three-sided pyramid, all of whose edges are equal. In any case, the number of nearest neighbors is the same as the usual chemical valence of the element; hence the name.

In the case of quartz the arrangement is similar, except that there is an oxygen atom between every pair of silicon atoms. When quartz is melted these groupings seemingly do not break up, and when the liquid is supercooled to quartz glass the little pyramids remain, but have not time or energy to return to the regular arrangement in the crystal and hence stay turned in various random positions.

Structure of Supercooled Liquids

Now we have gotten back to the supercooled, apparently solid substances with which the last chapter ended and have learned something of the more important properties of the gaseous, liquid, and solid state and of fluids, which include the first two, even when the liquid has become so hard that we would call it a solid were it not for its lack of crystallinity.

Specific Heat

THE HEATING AND MELTING of metals is a fundamental metallurgical process. At the absolute zero the atoms of a crystalline solid stand at rest. If we impart heat energy to the crystal, we cause the atoms to vibrate about the mean positions, producing what our sense of touch, or a suitable thermometer, recognizes as an increase in temperature, and also causing the object to increase in size. One might, at first, regard the amount of heat required for a given elevation of temperature or the increase of length accompanying this change as experimental constants. If so, they would be found to change with temperature.

Specific Heat

The amount of heat (in calories) required to raise the temperature of 1 g of a substance 1°C is called its *specific heat* and is represented by c ; that to raise the temperature of 1 g mol 1°C is called the *molar specific heat* and is represented by C . Ordinarily we heat or cool substances at constant pressure, usually atmospheric, and since the crystalline body does work by expanding against external

pressure, the heat absorbed is not only that manifested as a change in temperature but also the heat equivalent of this mechanical work, unless the pressure is zero. The specific heats at constant pressure, C_p or c_p , are thus greater than C_v or c_v , the specific heats at constant volume. In solids the latter would be difficult to observe experimentally. In the case of gases, however, C_v or c_v would represent the specific heat of the gas enclosed in a bottle of fixed size, inside which the pressure would of course rise with increasing temperature.

Not satisfied with experimental values, mathematical physicists have tried to deduce specific heats from theoretical considerations of the kinetic energy of atoms. It was long known that the atomic specific heat C_p of many substances tended to approach the same value, 6.2 cal/g atom, with rising temperature. This was the law of Dulong and Petit.

Nernst and Lindemann and Einstein attempted mathematical deductions concerning the relation of specific heat and temperature of isotropic substances, that is, substances whose properties are the same in all directions. This condition is well fulfilled by substances having simple cubic lattices and practically so by face-centered and body-centered cubic and even by hexagonal close-packed crystals.

Debye Function

The best attempt at the required solution was made by Debye. The fundamental assumption is that in a crystalline body the atoms do not vibrate at random but as part of a single system, as a tuning fork or violin string vibrates, except that vibration in three directions is possible. Assumptions are necessary as to the distribution of different vibrational frequencies, corresponding to the existence of overtones in a musical note, and limitations must be considered when the wave length becomes comparable with interatomic distances. Debye's assumptions

are now known to be oversimplified, but his results have been surprisingly close to observed facts.

The expressions are somewhat formidable, but the reader may wish to refer to this very important equation, even if he will use it only in the form of a graph.

According to Debye, the per atom specific heat of a symmetrically crystalline substance is

$$C_v = 9k \frac{1}{x_0^3} \int_0^{x_0} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (1)$$

when

$$x = \frac{h\nu}{kT} \quad \text{and} \quad x_0 = \frac{h\nu_{\max}}{kT}.$$

For gram atom substitute R for k .

We meet here some new concepts, which is one reason for introducing the equation. Planck's quantum of action h is a universal constant, independent of relativity considerations. It represents energy times time, and this is equivalent to saying that it has the dimensions of moment of momentum, a well-known concept in dynamics. Its numerical value is 6.6236×10^{-27} erg-sec or 1.5828×10^{-34} cal-sec. It appears in many radiation equations. The frequency of vibration is ν , and k is a constant called Boltzmann's, related to the gas constant R . It has the same relation to a molecule that R has to a gram molecule. Hence $6.06 \times 10^{23} k = R$.

The determination of the values of ν and their maximum is part of the fundamental Debye assumption. What makes the whole concept practicably workable is that $1/x_0$ can be written as T/θ_D . The Debye temperature, θ_D , could be derived from the elastic constants of the material. More simply it may be regarded as the absolute temperature at which $C_v = 5.67$. The specific heat of all substances to which the Debye function applies is the same when the ratio T/θ_D , its absolute temperature, to its Debye temperature, is the same. Usually the Debye function is

expressed as a graph (see Fig. 4-1), using T/θ_D as the abscissa and C_v as the ordinate. For any substance whose θ_D is known, from tables or otherwise, a given absolute temperature is quickly translated into the appropriate T/θ_D , and the atomic specific heat at constant volume is

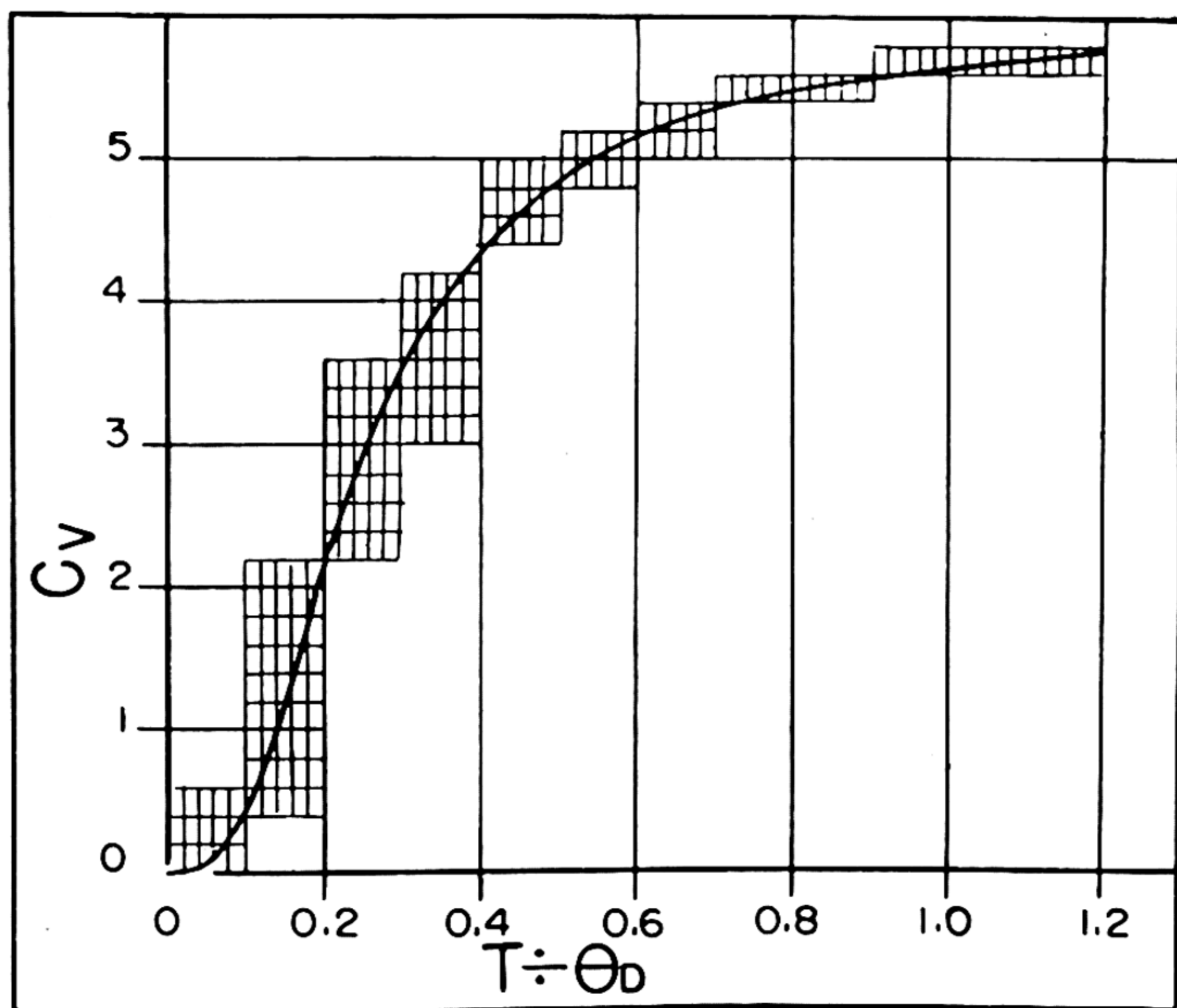


FIG. 4-1. Debye Function.

read off. Unfortunately, the metallurgically important elements iron and carbon (as graphite) do not conform to the Debye function. For the latter, Lewis and Gibson found the Debye relation to hold if $(T/\theta_D)^{0.789}$ is used instead of T/θ_D .

An important characteristic of the Debye function is that when T/θ_D becomes very small, at low temperature,

$$C_v = 464.5 \left(\frac{T}{\theta_D} \right)^3, \quad (2)$$

which has advantages when one wishes to make deductions concerning entropy, a subject to be referred to later.

Kopp's Rule

The molar specific heat of a compound is usually very nearly the sum of the atomic specific heats. This is known as Kopp's rule. If some of the elements (chlorine and bromine, for example) are not normally symmetric crystals at the temperature under consideration, in the corresponding salts (say of the alkali metals) the atomic heat of the element is the same in all compounds, and its value is obtainable by deducting from any known molecular heat the atomic heat of the metal.

Specific Heats at Constant Volume and at Constant Pressure

In all cases we have been calculating specific heats at constant volume when we are much more concerned with those at constant pressure. The physicist finds the former constant easier to compute but difficult to determine. It can be shown that

$$C_p - C_v = T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial P}{\partial T} \right)_v. \quad (3)$$

Here C_p and C_v are the atomic (or molar) specific heats at constant pressure and volume, respectively, T is the absolute temperature, $\left(\frac{\partial V}{\partial T} \right)_p$ is the rate of change of the atomic molar volume with temperature, the pressure remaining constant, and $\left(\frac{\partial P}{\partial T} \right)_v$ is the rate of change of pressure with temperature that will keep the substance at constant volume. Thus $\frac{\partial V}{\partial T}$ is an experimental constant since $\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)$ is the coefficient of cubic thermal expansion of

the substance. Similarly, $\left(\frac{\partial P}{\partial T}\right)_v$ can be derived from the ratio of measured compressibility of the substance and its thermal coefficient of cubic expansion. In calories Equation (3) is equivalent to

$$C_p - C_v = 0.02423 \frac{\alpha^2 V T}{\beta}, \quad (4)$$

where α is the coefficient of thermal expansion, $-\beta$ the coefficient of compressibility, T the absolute temperature, and V the atomic or molar volume.

Both α and β are functions of temperature and pressure. For crystalline solids the coefficient of thermal expansion of a given substance is directly proportional to its specific heat as shown by Grüneisen. He finds that

$$\alpha = - \frac{\gamma \beta C_v}{V_0}, \quad (5)$$

where α , β , and C_v have the previous meaning, V_0 is the atomic (or molar) volume of the solid at zero temperature (absolute) and pressure, and γ may be regarded as an experimental constant of the substance. Gamma has a theoretical relation to the compressibility of the substance:

$$\gamma = - \frac{1}{6} - \frac{1}{2} \frac{d \ln \beta}{d \ln V}, \quad (6)$$

where \ln signifies the natural logarithm. This relation is useful for substances of known compressibility, $-\beta$.

For emphasis let us review the first sentence of this chapter, which means that the heat content, sometimes given the impressive name enthalpy, of a crystalline solid is zero at the absolute zero. It is also apparently always true that the specific heat is zero. These facts are parts of the Nernst heat theorem, sometimes called the third law of thermodynamics.

Changes of State and Latent Heat

WHEN HEAT IS ADDED to a crystalline solid its temperature rises in accordance with the rate of heat input and the specific heat, which is a function of temperature. The heat absorbed in raising the temperature from T_1 to T_2 can be computed accurately only by evaluating:

$$H = \int_{T_1}^{T_2} C_p dT.$$

Latent Heat of Fusion

At a certain temperature the crystal ceases to heat but absorbs heat isothermally (that is, at constant temperature) and changes from the solid to the liquid state. The change in pure substances is usually assumed to take place at an exactly constant temperature. Its reverse, the freezing of a liquid, can, however, be suppressed to abnormally low temperatures, and the melting point can in principle be raised a trifle, a matter which we shall consider more in detail in a study of supercooling.

The heat absorbed in melting, corresponding to the energy required to break the bonds holding atoms in their crystalline positions, is called *latent heat of fusion*; or, with

reference to a gram atom or a gram molecule of a substance, this heat is called the *atomic or molar latent heat*, represented by the Greek letter lambda (λ) or by L_f .

Trouton's Rule

This is a most important constant in the study of equilibria in alloy systems and may be regarded as an experimental constant specific to particular substances. A principle especially applicable among the metallic elements is that the quotient obtained by dividing the latent heat of fusion by the melting point is very nearly the same for many metals.

Now the heat absorbed in an isothermal reversible process divided by the (constant) temperature at which the process takes place is called the *entropy* of the process or the change of entropy corresponding to the change of state. In connection with gram atoms the entropy S_f of fusion is, then,

$$S_f = \frac{L_f}{T_f}, \quad (1)$$

which is usually very near 2.2 cal/g mol. T_f is, of course, the absolute temperature of fusion. The rule is called Trouton's and is extremely useful in approximating the latent heats of fusion of metallic elements whose melting point is often easier to determine than the latent heat.

Attempts have been made to calculate the specific heat of liquids somewhat after the manner of the Debye function. The studies do not seem to have led to any very practical results. The specific heats of liquids are thus, for the engineer, still experimental constants, and unfortunately they are in many cases not known as well as one could wish.

Vapor Pressure

If we heat a liquid more and more, that is, increase the mean kinetic energy of its molecules, some molecules that have absorbed more than their share of energy move with

such velocity as to leave the liquid and mix with the gas phase. After a time some drop back while others bound out, and for every temperature there is some specific concentration of molecules in the gas when the two processes balance, the inbound molecules just equaling the outbound in a given time. A definite number of molecules in a gas, at a given temperature and pressure, means a given partial pressure due to these molecules and is called the *vapor pressure* of the liquid substance at the particular temperature.

When the vapor pressure becomes equal to the pressure on the system, usually 1 atmosphere, the substance boils. Solids also have a vapor pressure, but this is generally low.

Clausius-Clapeyron's Equation

The vapor pressure of a liquid changes with the temperature. The relation was the first one worked out theoretically in physical chemistry and is named for the two discoverers the Clausius-Clapeyron equation. It says that

$$\ln p = \frac{L_v}{R} \left(\frac{1}{T_b} - \frac{1}{T} \right). \quad (2)$$

Here $\ln p$ is the natural logarithm of the vapor pressure in atmospheres, L_v the latent heat of vaporization of a molecule of the substance, R the gas constant, T_b the boiling point of the substance at a pressure of 1 atmosphere, and T the temperature. As always we mean absolute or Kelvin temperature. Ostwald showed that vapor pressure does not change in any important degree with changes of total pressure.

There is also a Trouton's rule, similar to that for the relation of melting point to latent heat of fusion, which says that the entropy of vaporization of all substances is similar. The value is about 22 cal/mol at the normal boiling point. More uniform values are obtained if vaporization takes place under such conditions that there is 0.025 mol/liter of

gas. The entropy in such cases is pretty uniformly 27 cal/mol. Note that no matter how high the temperature gets, $\ln p$ still has a finite value that cannot exceed

$$\ln p = \frac{L_v}{RT_b}.$$

Taking 22 as the entropy of vaporization, we find that the maximum value is

$$\ln p = \frac{22}{R} = 11 \text{ (approx.)}.$$

The approximate constancy of the vapor pressure of low-boiling metals at high temperature has been verified by Leitgeb, who found a reasonable agreement with the calculations.

Specific Heat of Gases

The liquid having been vaporized, we are concerned with the molar, that is, the atomic specific heat of monatomic gases, which include the noble gases and presumably most metallic vapors. (The vapors of the alkali metals are diatomic.) It is $\frac{3}{2} R$ or 2.98 cal/°K at constant volume and $\frac{5}{2} R$ or 4.95 cal/°K at constant pressure for all substances.

The kinetic theory implies that C_v for diatomic gases should be $\frac{5}{2} R$ and for triatomic $\frac{6}{2} R$, and that $C_p - C_v = R$ in all cases. Monatomic molecules are limited to simple translational motions, while molecules of several atoms can have vibrations of their atoms in the direction of the line joining them and also can have kinetic energy of rotation about their center of gravity. Rotational energy is lacking in atoms because the small size of the nucleus makes its moment of inertia negligible. The net effect for diatomic molecules of gas is that specific heats at very low temperatures are but slightly increased above the calculated value of $\frac{5}{2} R$ for C_v , but as the temperature rises rotational motion adds an ever-increasing amount, which may reach a maximum of $2R$, to the specific heat.

For most substances not containing hydrogen, the latter addition is approximately correct at ordinary temperatures and above. It must also be remembered that many polyatomic gases dissociate into monatomic gases at high temperatures, with a corresponding absorption of heat. Thus iodine is triatomic near its room pressure sublimation temperature and monatomic at very high temperatures.

Hess's Rule

This groundwork should suffice us in determining the total heat capacity of any substance at any temperature.

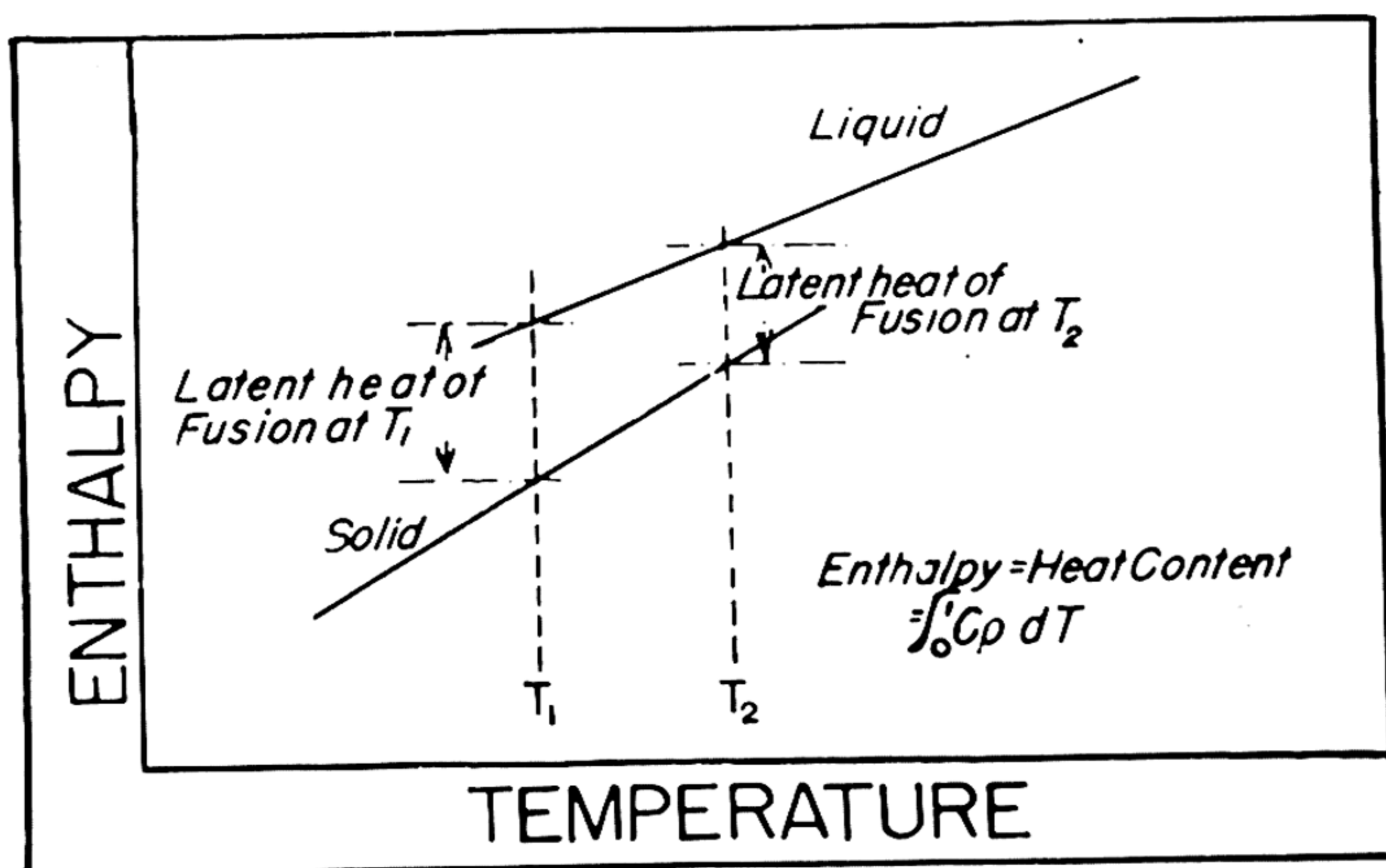


FIG. 5-1. Change of Latent Heat of Fusion with Temperature.

It may be well to emphasize that the heat required to bring any system from one state to another, involving changes of pressure, temperature, or physical state or chemical reactions, depends only upon the initial and final states and not at all upon the path by which the system goes from one state to another (Hess's rule). As a consequence such a property as the latent heat of fusion is a function of temperature (at constant pressure) if C_p is not the same for

the solid and liquid. Assuming (Fig. 5-1) C_l and C_s to be the values of C_p for the liquid and solid, neglecting changes in their values with temperature, and assuming L_1 and L_2 to be the latent heats of fusion at temperatures T_1 and T_2 , one may convert the solid at T_1 to the liquid at T_2 by first heating the solid from T_1 to T_2 and then melting it, when the heat absorbed per mol would be

$$C_s(T_2 - T_1) + L_2.$$

Or, one might melt the solid at T_1 and heat the liquid to T_2 , when the heat absorbed per mol would be

$$L_1 + C_l(T_2 - T_1)$$

and the two must be equal. Hence,

$$L_2 = L_1 + (C_l - C_s)(T_2 - T_1). \quad (3)$$

Free Energy and Equilibrium in Single-Component Systems

THE GROUNDWORK has now been laid for a study of equilibria, for we have just seen that there are conditions under which a substance can coexist in the solid and liquid states, or as a liquid and a gas. Imagine two containers containing a given substance and connected by a closed valve; in one the substance is in the liquid state and in the other it is in the solid; both are at the same temperature. The vapor pressure of the solid and liquid will be quickly reached in the two containers. If we then open the communicating valve to equalize the pressure, some vapor will pass from the container of the higher vapor pressure to that of the lower. The pressure in the container containing the substance in the state of lower vapor pressure will become adjusted to the proper value by the deposit of some of the material from the gas in the form in which the substance exists in that container, and some substance will vaporize in the other container.

A repetition of this process would finally transfer all of

the substance to the container in which it exists in the state of lower vapor pressure. At one temperature the vapor pressure of the two phases or states, solid and liquid, would be the same, and neither would be converted into the other by the procedure imagined above because no vapor would flow when the valve was opened. The two phases would be in equilibrium and the substance would be at its melting (or freezing) point. The state of lowest vapor pressure, if there is a difference, is the equilibrium state, and any other state, of higher vapor pressure, will spontaneously go over to it if it has the opportunity.

Sometimes the change of state cannot go on except very slowly, so that the unstable state may exist for an enormous time without detectable change. Such apparent but spurious equilibriums are called metastable.

Free Energy and Entropy

It is quite convenient to study simple equilibriums from a consideration of vapor pressures. For practical purposes other criteria derived from the same considerations by mathematical reasoning are more useful. Josiah Willard Gibbs originated a concept that he originally called the thermodynamic potential and that has later been renamed *free energy*. From the manner of derivation of this constant, the two great fundamental natural laws—(1) that energy cannot be created or destroyed, and (2) that energy tends to take forms making it less and less useful for doing mechanical work (that is, becomes degraded)—require that any process proceed spontaneously in the direction of reducing the free energy of the system (in other words, of the materials in which chemical and physical changes are being studied).

At constant pressure, substances have a property called free energy, designated by F and usually expressed in calories per mole, that is, gram molecule. This property measures the mechanical work recoverable if the material

is cooled to the absolute zero. It is calculable from the equation

$$F = H - TS. \quad (1)$$

The heat content H , which is mathematically $\int_0^T C_p dT$, is best found by measuring the area between the absolute zero and the working temperature T ($^{\circ}\text{K}$) under the Debye curve, or if necessary, some other curve in which specific heat at constant pressure is plotted against temperature.

Then entropy S is $\int_0^T \frac{C_p dT}{T}$ and is the area under a curve correlating C_p with $\ln T$ (the natural logarithm). Since $\ln 0 = -\infty$, one cannot measure the entire area but can measure that down to, say, 3°K and add an amount calculable on the assumption that C_p is proportional to T^3 as discussed under the specific heat of crystalline substances in Chapter 4, Equation (2). All this assumes that the substance is in the state stable at 0°K .

A somewhat clearer picture of the significance of entropy than can be had from its mathematical definition may be obtained from the following discussion. The amount of mechanical work recoverable from a given amount of heat energy depends not only on the amount of that energy but on the temperature level at which it is available. This is analogous to the fact that the amount of work a given amount of water can do depends on the level at which it exists. Only a process terminating at the absolute zero could convert all the heat content of a body into mechanical work. Entropy is a convenient way of recognizing how much of heat energy is unavailable. This may seem an awkward way to reach a solution, but it has been found the most convenient procedure when calculations involving this availability or lack thereof are to be made.

When the substance melts (or boils) without change of temperature the entropy of that change is the latent heat, equal to H , divided by the temperature. Expression (1)

then reduces to zero for ΔF , the change in free energy. Two states of the same substance are thus in equilibrium if their free energies are equal. Otherwise that state disappears which has the higher free energy.

The value of F is related to vapor pressure by the formula

$$\Delta F = RT \ln \frac{p_2}{p_1}. \quad (2)$$

If at constant temperature two states of a substance have vapor pressures p_1 and p_2 , the change of free energy in passing from state one to state two is that indicated in the foregoing formula, where R is the familiar gas constant and T the absolute temperature.

For two states of equal vapor pressure, $\ln \frac{p_1}{p_2} = \ln 1 = 0$ and $\Delta F = 0$, representing equilibrium. If p_1 and p_2 are different (p_2 being the smaller) $\ln \frac{p_2}{p_1}$ is negative and so is ΔF ; that is, the free energy of the substance is decreased by passing from the state of higher vapor pressure to that of lower vapor pressure, temperature being constant. This is the mathematical parallel to the mechanical analogue described at the beginning of the chapter.

Returning to Equation (1), we know that we can recognize only changes in entropy, and so far we know nothing of its absolute value. It is quite reasonable, and can indeed be formally supported, that H , the heat content, is zero at the absolute zero. The TS term of Equation (1) is zero at the absolute zero if entropy is finite. The so-called Nernst heat theorem, which is becoming practically a third law of thermodynamics, leads to the conclusion that crystalline solids, in the form in equilibrium at absolute zero, have zero entropy at the absolute zero. If they are pure substances no degree of atomic disorder is possible. The entropy of crystalline solid solutions is very near zero at the absolute zero. Supercooled liquids have positive entropies at zero

which may, however, be quite small. The theorem is not applicable to gases.

This reasoning leads to the conclusion that the free energy of crystalline substances in their low-temperature equilibrium state is zero at the absolute zero, and hence Equation (1) can be applied directly for any temperature, it being proper to consider the entropy, at least of the crystals, as being too small for consideration. We are not especially concerned with entropies of gases, although these can be predicted from the so-called Sackur equations. The fact that these equations give negative entropies at the absolute zero is of no importance, since the gaseous elements are not perfect gases obeying the relation

$$pV = RT$$

when low temperatures are reached.

Free Energy versus Temperature and Pressure

The free energy of a substance changes with temperature and pressure according to the equations

$$\left(\frac{\partial F}{\partial p}\right)_T = V \quad (3)$$

and

$$\left(\frac{\partial F}{\partial T}\right)_p = -S. \quad (4)$$

These differential equations say: Equation (3), that the rate of change of free energy with pressure, temperature remaining unaltered, is equal to the molar volume of the substance and, Equation (4), that the rate of change of free energy with temperature, pressure remaining constant, is numerically equal to the entropy but of opposite sign.

The entropy is of course a function of specific heat and temperature; hence the rate of change is constant over a minute pressure range only. For the present we are concerned mainly with the fact that since entropy is always

positive, free energy always decreases with increasing temperature. Similarly, since V is a function of pressure, the rate of change of free energy with respect to pressure is constant only over a minute range but is always positive, as is the molar volume. The molar volume of condensed systems (solids or liquids) is small, so that the free energy

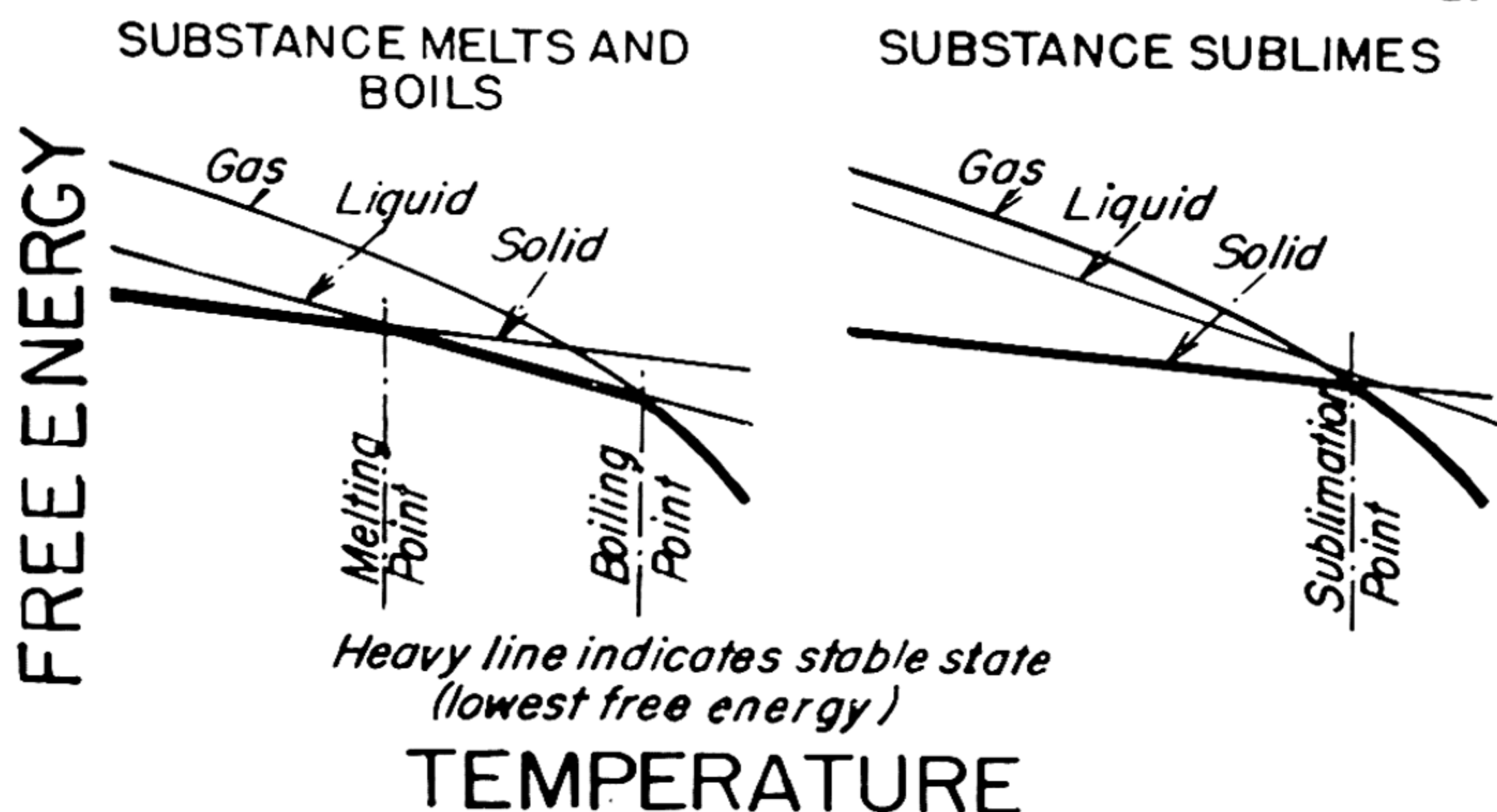


FIG. 6-1. Free Energy of a Substance in Three States.

of such substances increases very slightly with pressure, but that of gases increases greatly. For a perfect gas Equation (3) would become

$$\left(\frac{\partial F}{\partial \ln p} \right)_T = RT; \quad (5)$$

that is, free energy (at constant temperature) is a linear function of the natural logarithm of pressure.

If we had only to consider freezing points or boiling points of pure substances at constant pressure, all this deduction of free energy and saying that two states of the same substance are in equilibrium when their free energies are equal would be quite superfluous and represent "much ado about nothing." It will presently turn out, however, to have much to do with the freezing of solutions. Molten

metals are almost always complicated solutions, and the temperature of freezing usually covers a range. The composition of the solid forming as the solution cools can best be described in terms of this free energy.

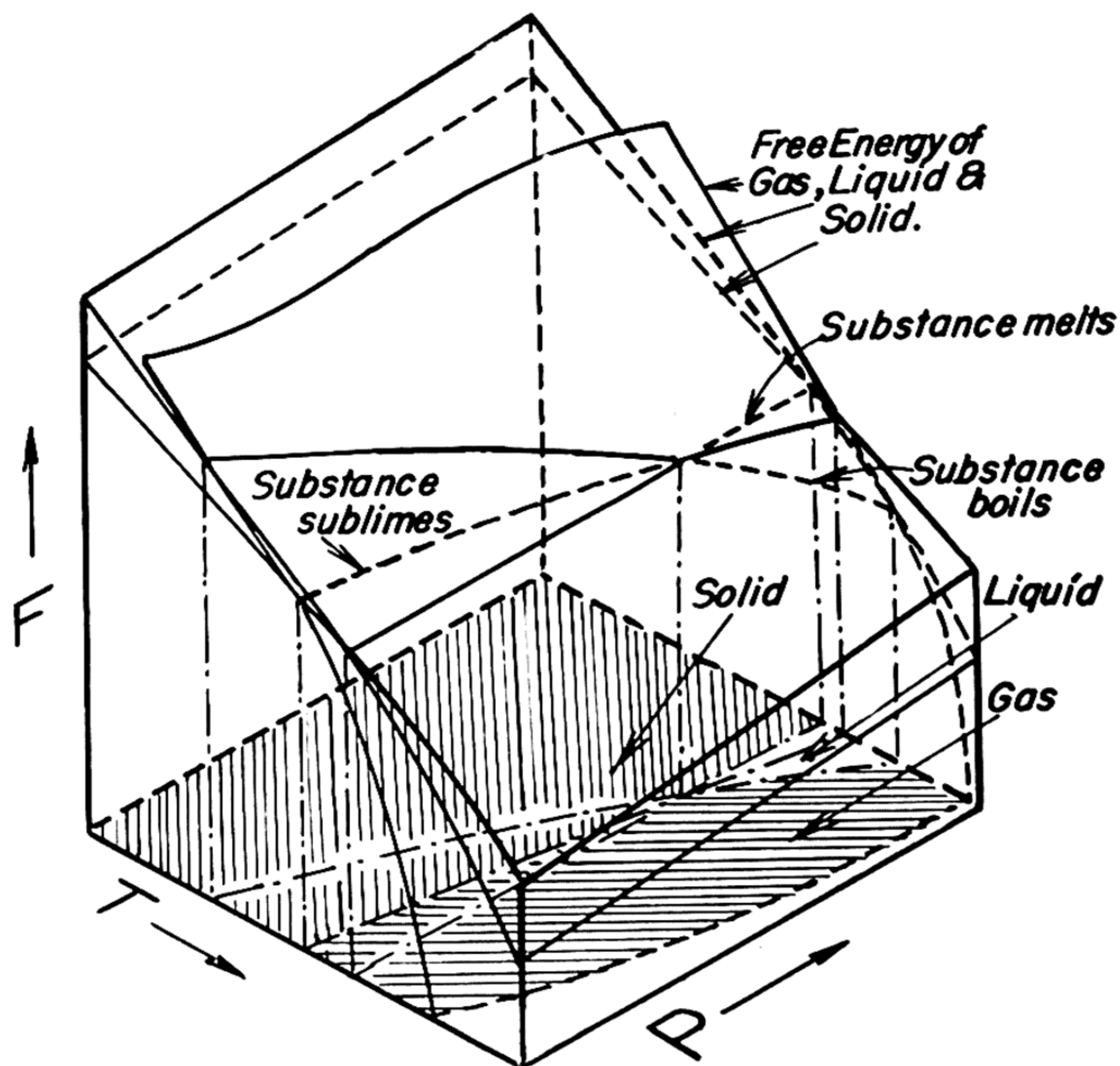


FIG. 6-2. Temperature-Pressure-Free Energy Relation of the Three States of a Substance.

Also, free energy furnishes an explanation of the phenomenon of supercooling when substances remain liquid far below their normal melting points.

The free energy relations of a substance at constant pressure in its three physical states are shown in Fig. 6-1. The stable state is always that of lowest free energy. Fig. 6-2 is an isometric projection of the same properties as a function of both temperature and pressure.

Free Energy and Binary Equilibrium

FREE ENERGY has still other important relations to what happens in freezing. Only pure substances, elements or chemical compounds and certain peculiar solutions said to be of *eutectic* composition, freeze without change of composition. In them the freezing process takes place at a definite temperature, and the solid and liquid states or phases are of the same composition. The solid eutectic is itself two-phased (in alloys of two components) but is of the same average composition as the liquid.

In all other cases there is a temperature range in which the metal is partly liquid and partly solid, that is, two-phased, and the two phases differ in composition. What these compositions are and what the freezing range is depends on certain free energy considerations discussed in the following paragraphs.

Partial Molal Free Energy

Fig. 7-1 represents some facts concerning the free energy of metallic solutions. The abscissas of the figure represent concentrations and the ordinates free energy (per molecule). At the left side of the figure the alloy is pure A, whatever

that may be, and at the right, pure B. Any vertical line between the two sides represents an alloy of a given composition. That halfway between the two sides represents equal numbers of molecules of A and B, $\frac{1}{3}$ of the way from the left, $\frac{1}{3}$ the molecules of A and $\frac{2}{3}$ of B, and so on. We

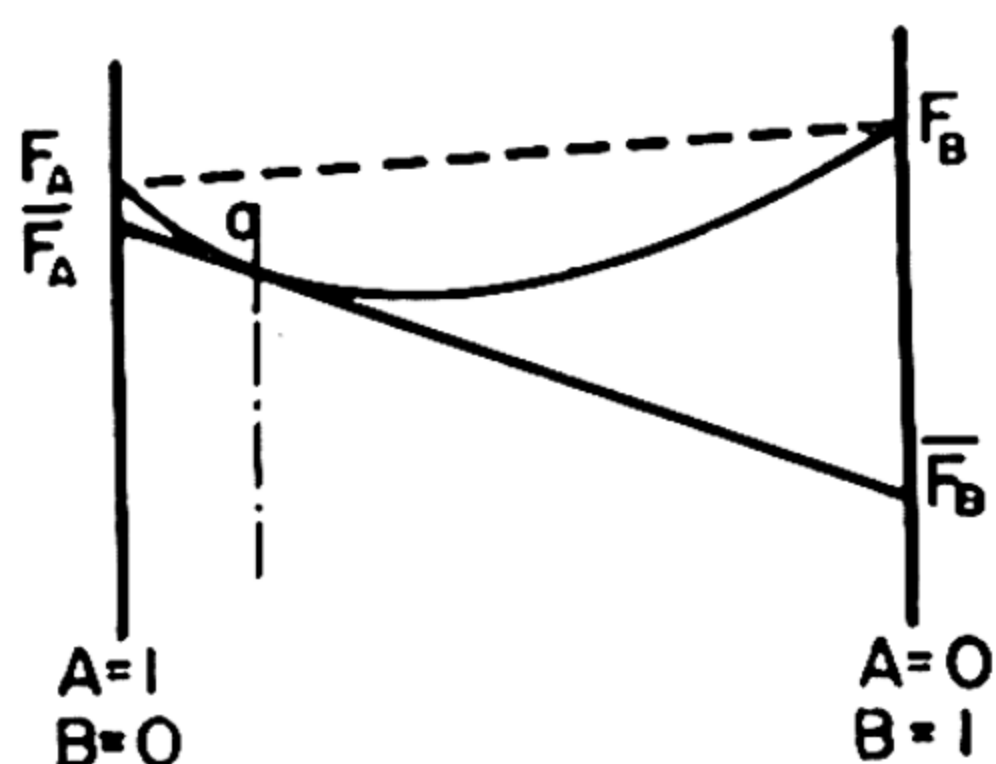


FIG. 7-1. Partial Molal Free Energy of Components of a Solution.

deal here not with the proportions by weight but with the molecular proportions. Assuming, not necessarily correctly, that the liquid metals are monatomic, that A is tin and B lead, whose atomic weights are in round numbers 119 and 207, respectively, then an alloy containing 119 parts by weight of tin and 207 of lead has 50 atomic (or molecular) per cent of each. An alloy containing equal parts *by weight* of each contains $1/119$ atoms of tin for $1/207$ atoms of lead; that is, 0.0084 atom of tin and 0.0048 of lead in a total of 0.0132. This is an atomic fraction of $48/132 = 0.365$ of lead and $84/132 = 0.635$ of tin (approximately).

At the left of the figure the free energy of pure liquid A is marked off, and at the right that of B. These are marked F_A and F_B . Now a mixture of the two liquids (if there were no solution and the mixture were merely like that of oil and vinegar in French dressing) would have for any composition the free energy represented by the dotted straight line joining F_A and F_B . If the metals dissolve in one another, like oil in gasoline, the principle that nature strives for the state of lowest free energy tells us that the free energy of the solution must be below the straight line for all compositions. During the process of mixing, heat is evolved and the free energy decreases. Let us assume it to be represented by the curve shown as a solid curve joining

F_A and F_B . The reader need not worry at this point as to how this curve becomes known; let him assume that it is known.

Consider now any point a on the curve and draw a tangent line as shown, intersecting the ordinates $A = 1$ and $B = 1$ at \bar{F}_A and \bar{F}_B . These two points mark what are called the *partial* molal free energies of A and B in a solution of composition a at the temperature for which the diagram applies. At this temperature and concentration only, the liquid behaves as though it were a mixture, not a solution, of A and B, having not their proper free energies, but fictitious ones corresponding to their partial values.

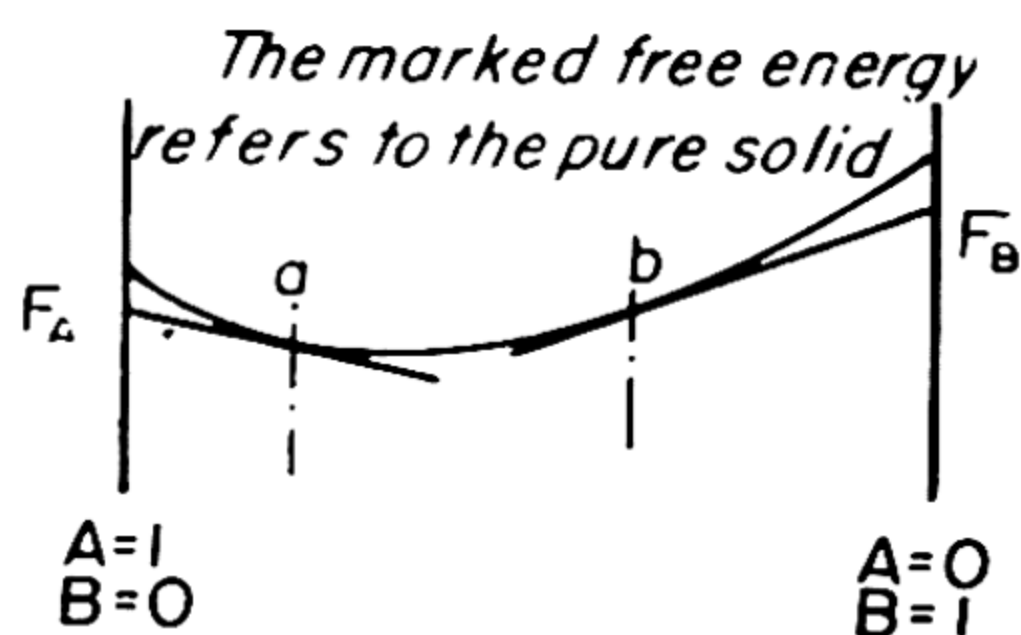


FIG. 7-2. Composition of a Liquid Solution in Equilibrium with Pure Solid Components.

By using these partial molal free energies we can describe readily the equilibrium conditions and hence the behavior on freezing for various metallic liquids.

Fig. 7-2 is an elaboration of Fig. 7-1 for an alloy of two metals that are insoluble in the solid state. Actually this condition may never be completely realized, but it is closely approached in the system antimony-lead. A temperature has been chosen such that the free energy of each metal in the solid state is lower than in the liquid state. Tangents to the liquid's free energy curve are drawn through the free energies of the two pure solids.

From the description of Fig. 7-1 it should be clear that at a the partial molal free energy of A is equal to the free energy of the pure solid A and similarly at b for B. Since then the free energy of A is the same, at this temperature, in the liquid of composition a and in the solid, no change in free energy of the system will occur if a very small proportion of the amount of A present is transferred from liquid to

solid and the composition a is in equilibrium with pure (solid) A and b with pure (solid) B.

At the temperature chosen, alloys of compositions to the left of a are mixtures of the solid A and the liquid of concentration a . The free energy of such a mixture, represented by the straight tangent, falls throughout below the

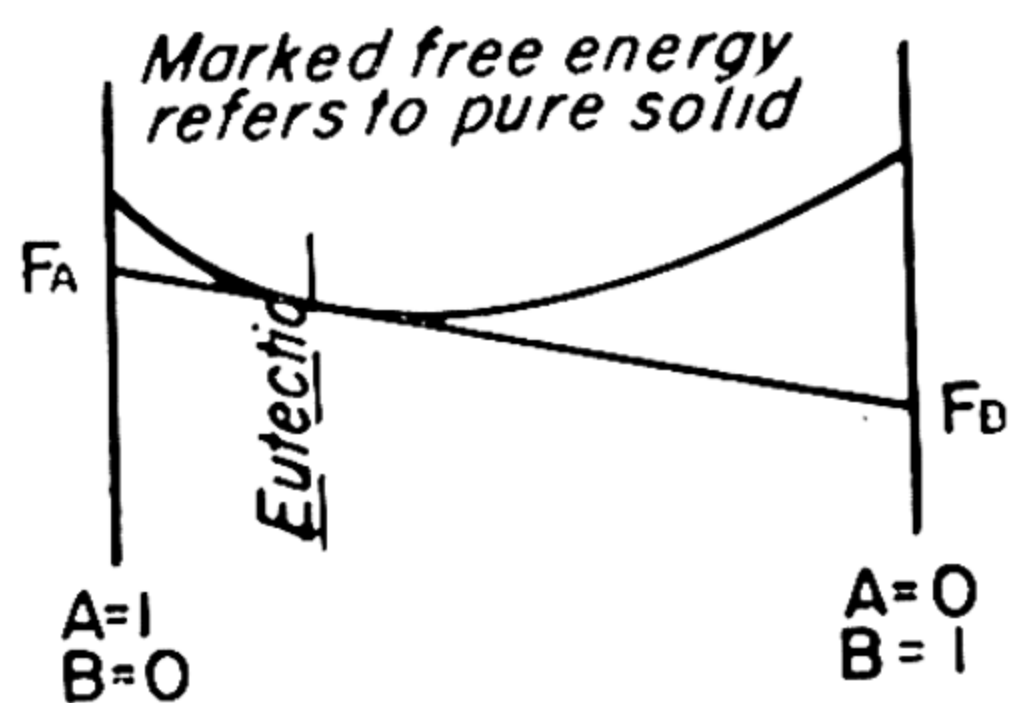


FIG. 7-3. Equilibrium at the Eutectic Temperature.

curve for the liquid. Between concentrations a and b the alloy is a liquid, and to the right of b it is a mixture of concentration b and pure solid B. If such a diagram is drawn for each of many temperatures and the concentrations a and b are plotted against temperature, a constitutional diagram results, showing the temperature at which freezing begins in relation to composition.

Under these conditions there will always be found one temperature, the lowest at which any liquid can exist, called the eutectic temperature, for which a diagram like Fig. 7-3 will be obtained, in which the curve becomes tangent to the straight line corresponding to a solid mixture of A and B. The concentration corresponding to the point of tangency is called the eutectic composition.

Van't Hoff's Isochore

An analytical solution can be developed, based on the same fundamental laws as the free energy concept. This states that if in the solid state A is insoluble in B, then

$$\ln X_B = \frac{L_{fB}}{R} \left(\frac{1}{T_{fB}} - \frac{1}{T} \right). \quad (1)$$

Here X_B is the mol fraction of B, L_{fB} the molecular heat of fusion of B, R the gas constant, T_{fB} the melting point of B

in $^{\circ}\text{K}$, and T the existing temperature. This relation is called van't Hoff's isochore.

If B is also insoluble in solid A and the solid state consists of a mixture of A and B, then there is another such equation for X_A .

Also, at the eutectic freezing point the sum of the mol fractions of A and B must be unity. One may then write*

$$\exp\left(\frac{L_{fB}}{R}\right)\left(\frac{1}{T_{fB}} - \frac{1}{T}\right) + \exp\left(\frac{L_{fA}}{R}\right)\left(\frac{1}{T_{fA}} - \frac{1}{T}\right) = 1. \quad (2)$$

A solution of this equation (best graphically) for T will give the eutectic temperature.

For our purpose it may be well to remember Trouton's rule that the ratio of atomic latent heat of fusion (calories) to melting point ($^{\circ}\text{K}$) is nearly constant at 2.2 and that R is practically 2. For T_E the eutectic melting point Equation (2) may then be written

$$\exp\left(1.1 - \frac{1.1T_{fA}}{T_E}\right) + \exp\left(1.1 - \frac{1.1T_{fB}}{T_E}\right) = 1,$$

or may be divided by $e^{1.1} = 3.004$:

$$\exp\left(-\frac{1.1T_{fA}}{T_E}\right) + \exp\left(-\frac{1.1T_{fB}}{T_E}\right) = 0.333. \quad (3)$$

The equation is shorter than Equation (1) and requires no knowledge of latent heats but may be in error to some extent.

It may be that the two components A and B are completely soluble in the solid state, nickel and copper for example. There are then two curves, such as in Fig. 7-1, one for a solid solution and the other for a liquid. If the temperature is in that range in which the system is completely liquid, the curve for the liquid state is entirely below that for the solid and the latter is of no interest here; or if

*The expression " $\exp(n)$ " is equivalent to " e^n ," e being the base 2.718 . . . of the natural system of logarithms; that is, $\exp(n) = \text{antiln } n$.

the alloy is completely solid, the free energy curve of the liquid is entirely above that for the solid and again we need not discuss the condition.

If the curves intersect, as for example in Fig. 7-4, we can see what the composition of the solid and liquid phases

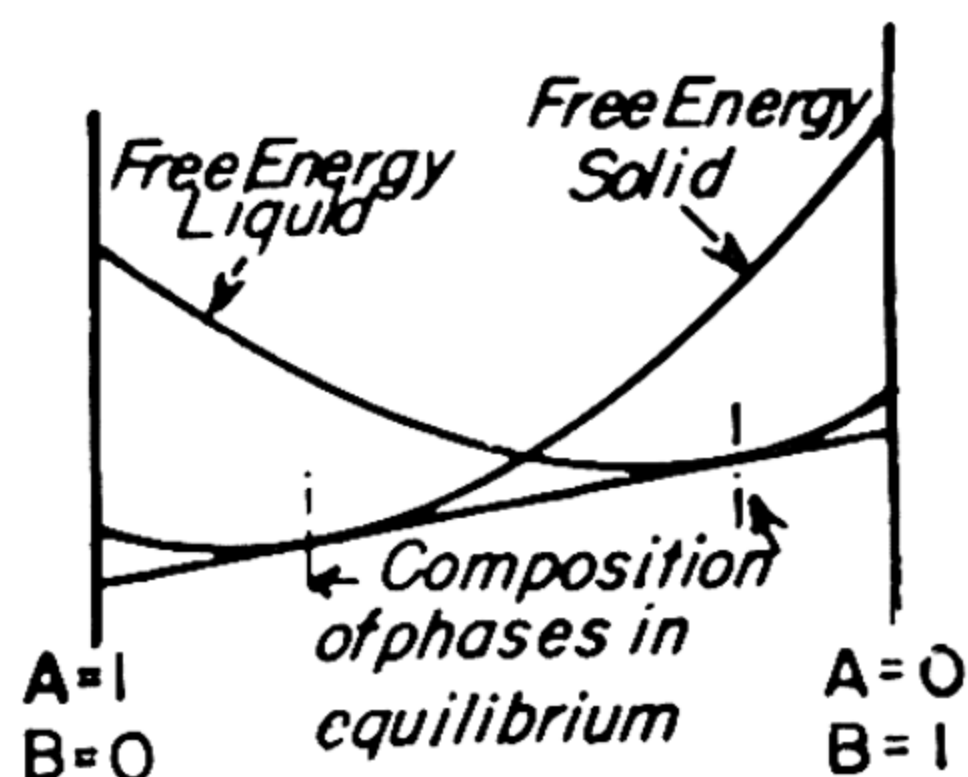


FIG. 7-4. Equilibrium Compositions of a Solid and a Liquid Solution.

will be at the temperature for which the diagram is drawn. If a single line be drawn tangent to both curves in Fig. 7-4, evidently the partial molal free energies corresponding to its ends are the same in the solid and liquid state for A and also for B.

Without repeating the details of the reasoning, evidently we may conclude that the two solutions are in equilibrium.

Van Laar's or Schroeder's Equation

Repeating the diagram for many temperatures would enable us to plot the constitutional diagram showing the temperatures at which freezing begins and ends, for all compositions.

Again, there is an equation (an elaboration of the van't Hoff isochore) called either van Laar's or Schroeder's, which says that

$$\ln \frac{X_{A_1}}{X_{A_2}} = \frac{L_{fA}}{R} \left(\frac{1}{T_{fA}} - \frac{1}{T} \right). \quad (4)$$

Here X_{A_1} is the concentration of A in the liquid and X_{A_2} in the solid. The other symbols have the usual meaning.

One may write also a similar equation for B and remember that at all temperatures $X_{A_1} + X_{B_1} = X_{A_2} + X_{B_2} = 1$.

This gives four equations for the four unknown concentrations that permit a solution.

As in the case of Equation (2), Equation (4) can be

simplified by substituting 2.2 for L_f/T_f for any substance. It then becomes

$$\ln \frac{X_{A_1}}{X_{A_2}} = 1.1 - \frac{1.1T_{fA}}{T}, \quad (5)$$

or

$$\begin{aligned} \frac{X_{A_1}}{X_{A_2}} &= e^{1.1 - (1.1T_{fA}/T)} \\ &= 3.004e^{-1.1T_{fA}/T}; \end{aligned}$$

similarly

$$\frac{X_{B_1}}{X_{B_2}} = 3.004e^{-1.1T_{fB}/T} = \frac{1 - X_{A_1}}{1 - X_{A_2}},$$

$$X_{A_1} = 3.004X_{A_2}e^{-1.1T_{fA}/T},$$

$$\frac{1 - 3.004X_{A_2}e^{-1.1T_{fA}/T}}{1 - X_{A_2}} = 3.004e^{-1.1T_{fB}/T},$$

$$1 - 3.004X_{A_2}e^{-1.1T_{fA}/T} = 3.004e^{-1.1T_{fB}/T} - 3.004X_{A_2}e^{-1.1T_{fB}/T},$$

$$3.004X_{A_2}e^{-1.1T_{fA}/T} - 3.004X_{A_2}e^{-1.1T_{fB}/T} = 1 - 3.004e^{-1.1T_{fB}/T},$$

$$X_{A_2}(e^{-1.1T_{fA}/T} - e^{-1.1T_{fB}/T}) = 0.333 - e^{-1.1T_{fB}/T},$$

$$X_{A_2} = \frac{0.333 - e^{-1.1T_{fB}/T}}{e^{-1.1T_{fA}/T} - e^{-1.1T_{fB}/T}}, \quad (6)$$

and likewise for the three other concentrations. All the constants on the right half of Equation (6) are known.

One may profitably take a quick look at some other forms of free energy curves. The curve in Fig. 7-5, falling entirely above the straight line joining its ends, has no realizable existence, at least under equilibrium conditions; neither substance is soluble in the other. Fig. 7-6 represents a case of limited solubility in the liquid state, copper and iron for example. Such curves permit drawing a common tangent at two points as shown. The middle por-

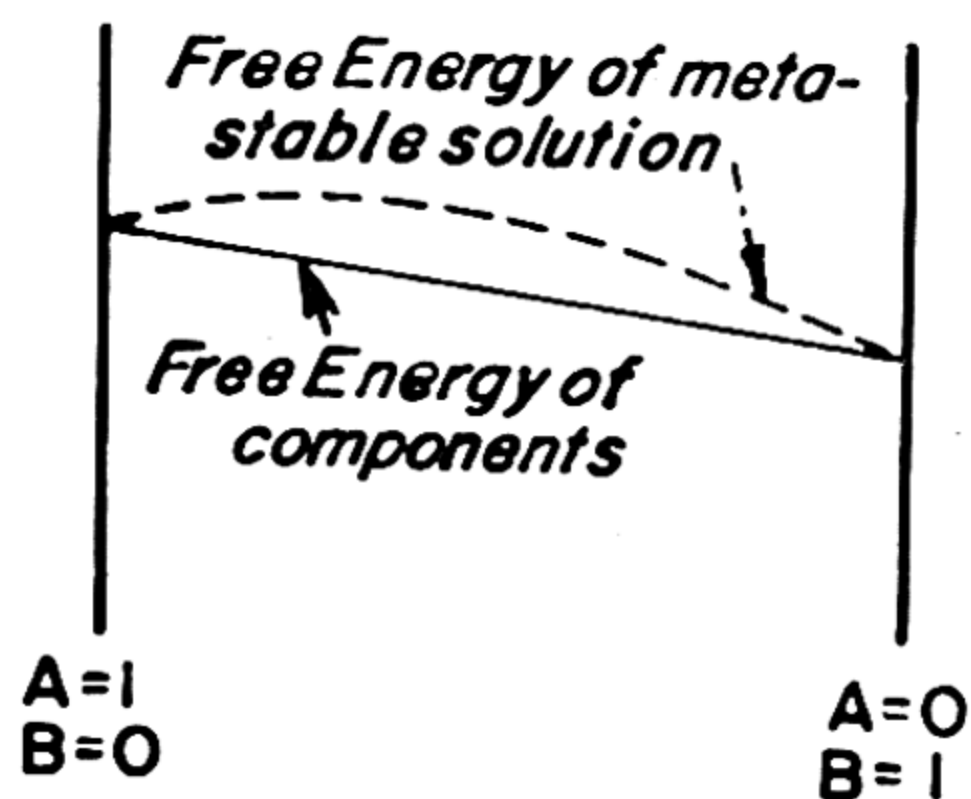


FIG. 7-5. Free Energy of a Metastable Solution.

tion of the curve, shown dotted, is not realizable. Between a and b the liquid consists of two layers or perhaps an emulsion, but at the ends solubility exists.

In Fig. 7-7, if the condition is as represented at the A end of the curve, the alloys to the left of a in concentration consist of pure solid A and liquid solution of concentration a .

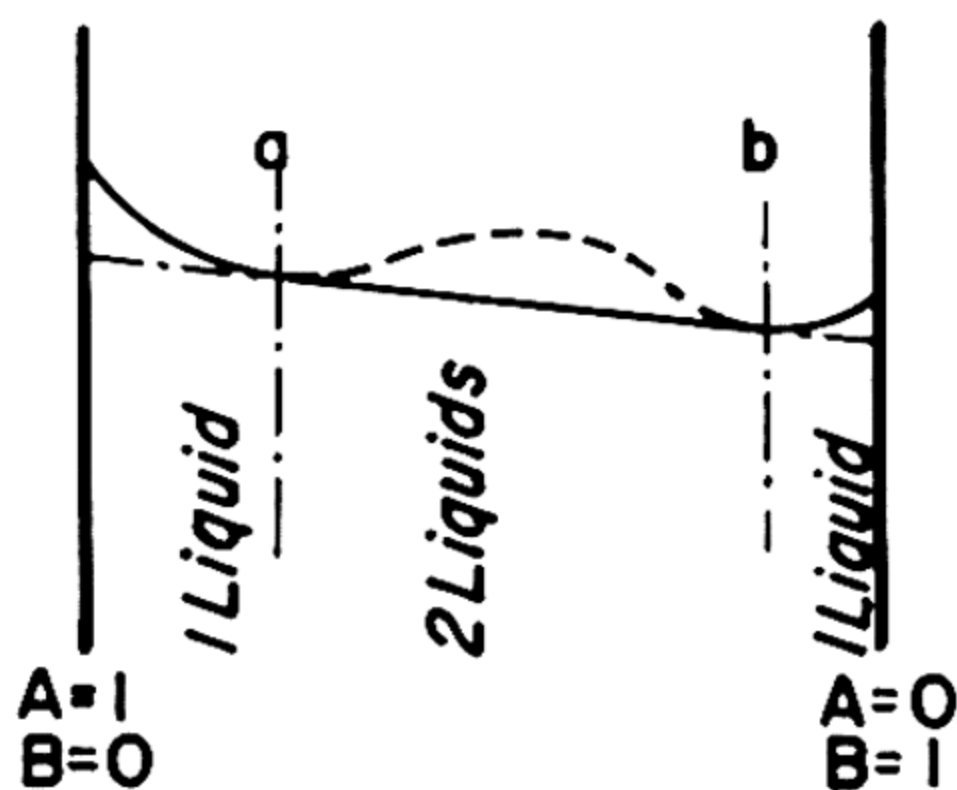


FIG. 7-6. Free Energy of a Liquid with a Miscibility Gap.

When solid solubility does not exist, the slope of the free energy curve for the solid state at $A = 1$ is flatter than the tangent to the curve for the liquid through the point representing the free energy of pure solid A.

It is not especially unusual for the two free energy curves to become tangent to one another at the last moment before the freezing point is reached (see Fig. 7-8), in which case their common tangent is at the same point and freezing is completed by a process in which liquid and solid have the same composition. This happens, for example, in the iron-chromium alloys at about 25 (weight) % chromium.

The situation with regard to the possibility of existence of three solutions at one temperature, but of course at different concentrations, could be considered and a three-dimensional model could be made

for a ternary system, paralleling the diagrams for a binary. For more than three components a model is no longer possi-

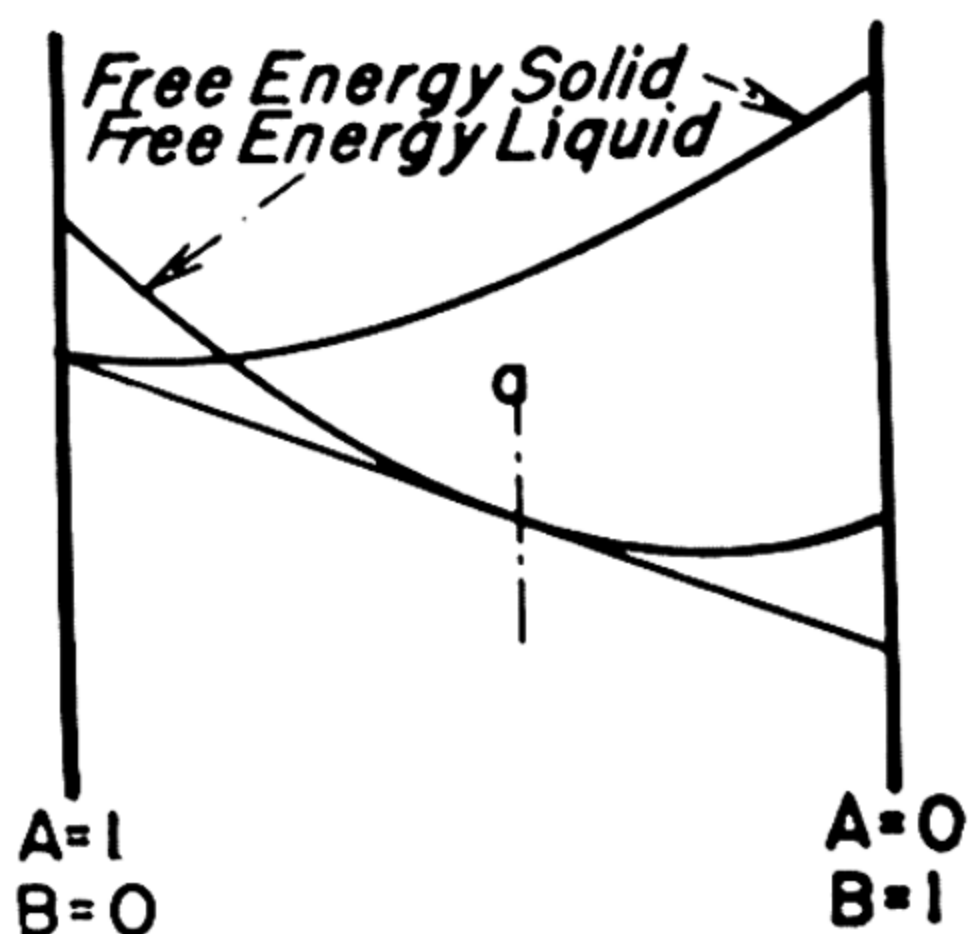


FIG. 7-7. Equilibrium of a Liquid Solution with a Pure Component of a Solid Solution.

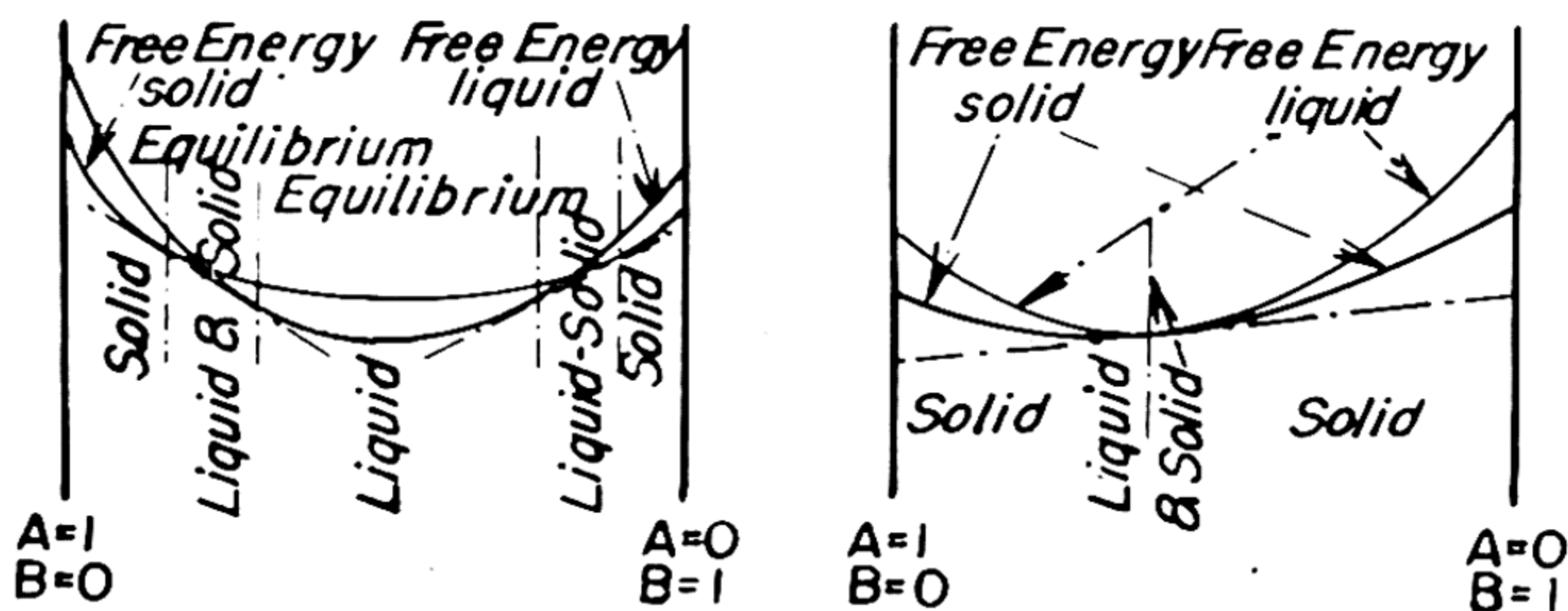


FIG. 7-8. Free Energy Relation of Solid and Liquid Solutions Having a Freezing Point Minimum. *Left*: Temperature in Partially Frozen Range; *Right*: Temperature at Minimum Freezing Point.

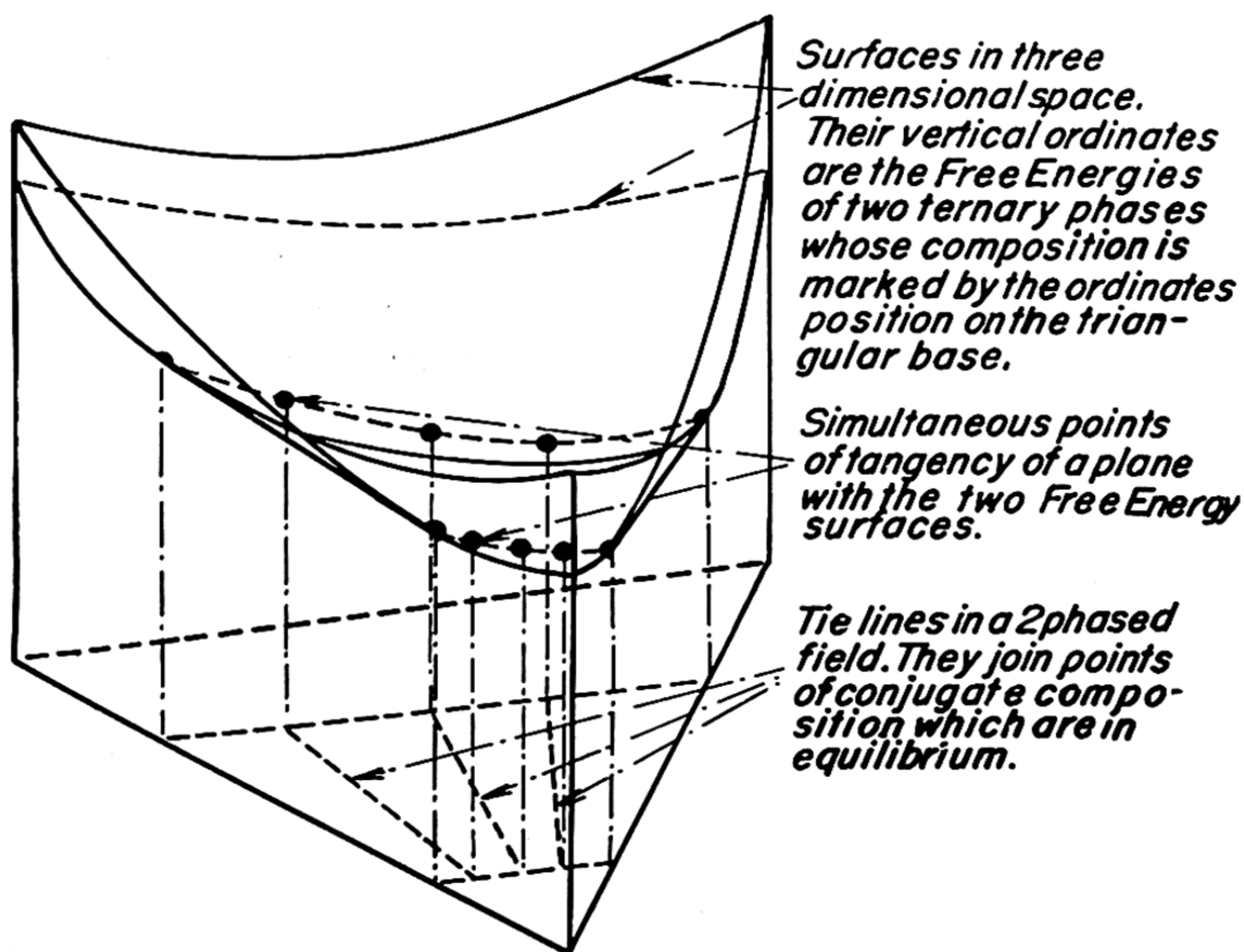


FIG. 7-9. Equilibrium between Solid and Liquid Ternary Solutions.

ble in three-dimensional space, and the facts could be expressed only in the form of equations, much more complicated than those of this chapter.

Fig. 7-9, which is no doubt self-explanatory, shows how similar constructions can be made in three-dimensional space for ternary systems.

Valence Electrons and Solid Solubility

Van Laar's Equation (4) does not assign any particular form to the solidus and liquidus curves in alloys showing limited solubility curves. Hume-Rothery, however, has pointed out that the depression of the beginning of freezing (liquidus) or its completion (solidus) in a given solvent by solutes having varying numbers of valence electrons is proportional to those numbers. Thus a given mol fraction of a solute with one valence electron depresses these lines half as much as the same mol fraction of a solute containing two valence electrons.

The form of the two curves is similar to that of van't Hoff's isochore Equation (1). The systems react as though solubility of valence electrons in the solid solution were the governing feature.

Supercooling

THE GRAY-IRON FOUNDRYMAN recognizes that if he cools his molten metal quickly, as by pouring it into an unusually thin section, or against a chill, he may get white cast iron instead of gray cast iron. This happens (by a mechanism that will be discussed in another connection) because the metal was supercooled in freezing. That is to say, it did not freeze at the expected temperature but remained liquid until a lower temperature was reached.

How great this lowering of the freezing point can be is shown in Fig. 8-1, after Schneidewind and d'Amico. The figure shows the measured freezing point at various distances along a wedge that tapered from about 3 or 4 in. in thickness to a rather thin edge. The thin sections, which cooled faster, had the lower freezing point.

How can such things be? Were we not told that freezing points are physical constants characteristic of given substances? Here a little theory helps. We turn to the concept of free energy that seemed so needlessly cumbersome earlier in this study. In Fig. 8-2 we draw two lines showing the free energies of liquid and solid metal as

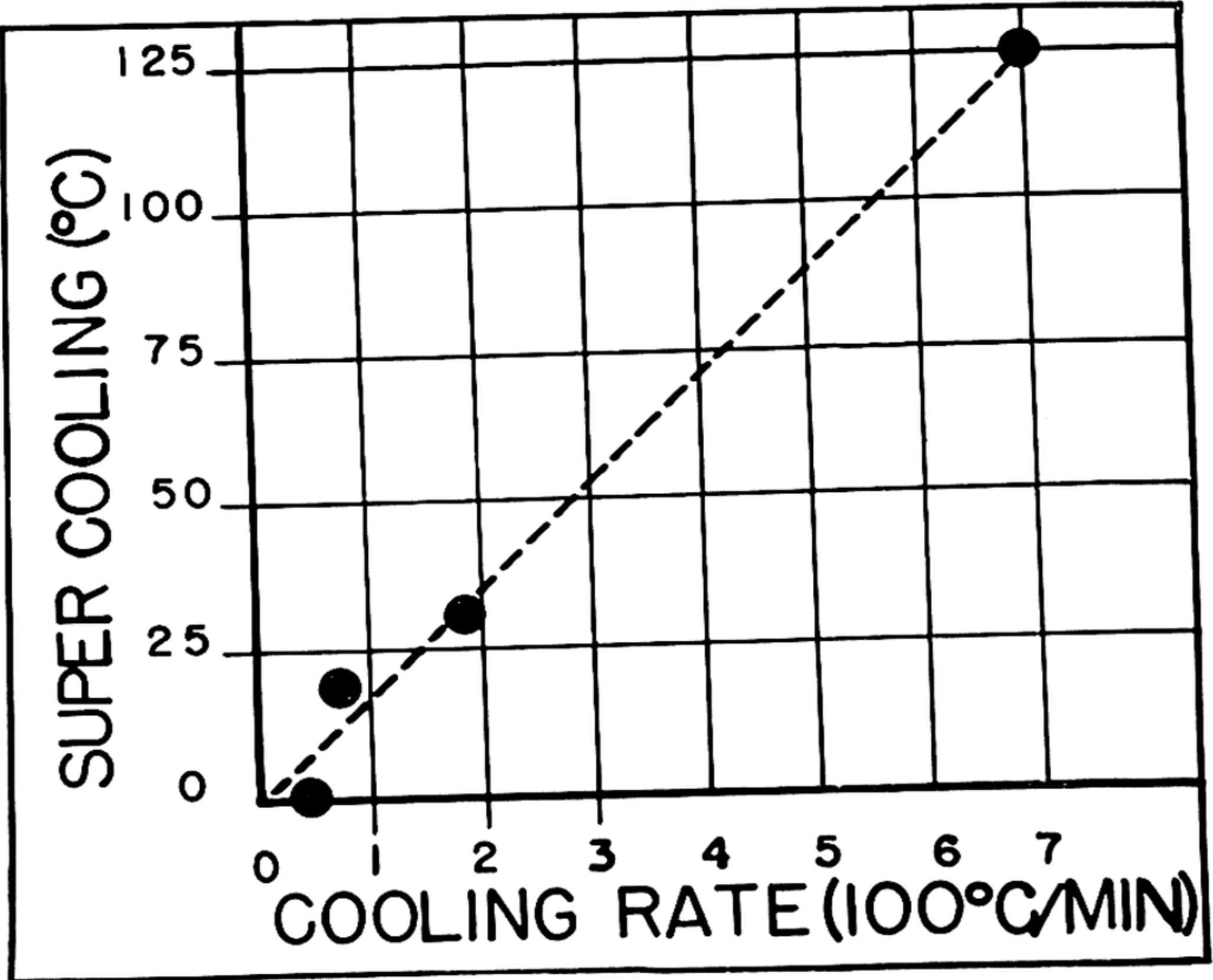


FIG. 8-1. Supercooling in Relation to Cooling Rate of Liquid Cast Iron. (After Schneidewind and d'Amico.)

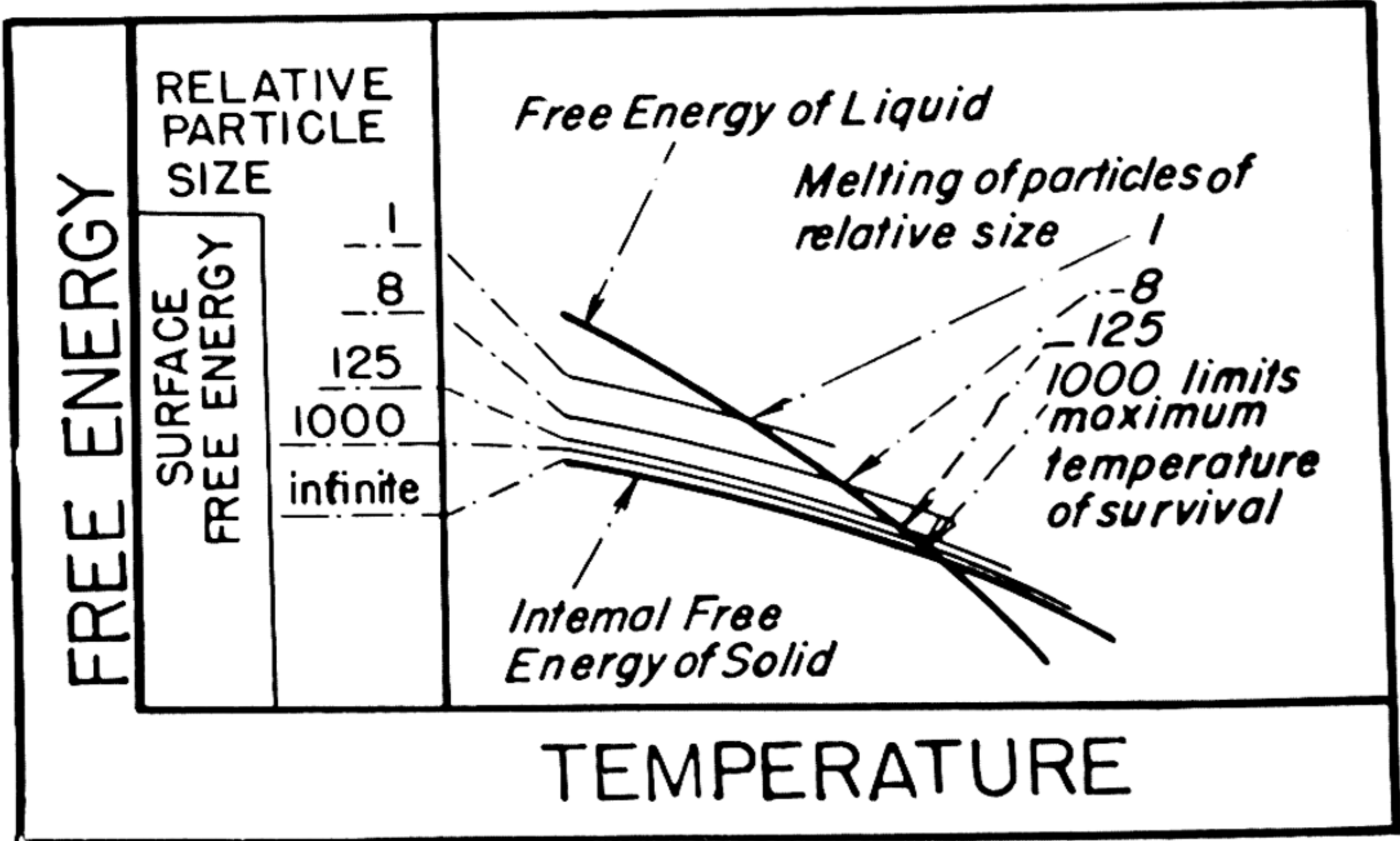


FIG. 8-2. Surface Free Energy and Supercooling.

related to temperature. For simplicity in explaining supercooling we will consider this to be a pure substance. It should have a single sharp freezing point as is shown by the intersection.

Surface Free Energy

This diagram leaves out another item contributing to free energy, which is called *surface free energy*. If a solid particle is floating in a liquid, the surface of contact tries to pull toward the center of the particle because atoms near the surface are attracted more strongly toward the solid, whose atoms are more densely arranged, than toward the liquid, where the atoms are further apart.

The effect is that work can be done by decreasing the surface of contact, which may be caused either by the particles becoming rounder or by their coalescing to form fewer and larger aggregates. This surface energy, being expressed customarily in calories per gram atom or molecule, is proportional to the surface area divided by the mass, or (of course, with a different numerical relation) to this area divided by the volume of the particle, which, assuming an equiaxed particle (one of nearly the same dimensions in all directions) is inversely proportional to the particle's diameter (or to the cube root of its volume). This surface energy acts as an increment to the solid's free energy, and, if the solid line of Fig. 8-2 represents the free energy of the solid in large pieces, a series of dotted lines can be drawn parallel to and above this line, representing the addition due to surface free energy for various sizes of particles (according to some arbitrary dimensional scale). The intersections of these lines with the free energy lines for the liquid then represent the melting points of very small particles of the several sizes. So far we have shown that the freezing point can be lowered, by small amounts, by making the solid particles smaller.

The freezing process begins by the accidental arrange-

ment of a number of atoms in the liquid in space in the pattern they would occupy in the solid. If the group is large enough so that its melting point is above the existing temperature, the arrangement remains permanently and attracts other atoms to it so that a crystal grows. If the group is, however, smaller than the size whose freezing point just exists, then, still by accident, its members disperse.

Of course the likelihood of forming small groups is better, by random chance, than that of forming larger ones. Therefore, as the temperature falls, more and more groups will remain permanently and continue to grow and finish the freezing process.

Consider now another matter: crystals can only grow so fast; the rate is called *linear crystallization velocity*. This probably does not vary much with temperature. As the crystal grows it gives off the heat that was required to melt it. A given number of crystals, of a given size, can therefore give off only the amount of heat corresponding to the rate of growth and the latent heat of fusion. If crystals are equiaxed, their areas are proportional to the square of their diameters, or to the $\frac{2}{3}$ power ($\sqrt[3]{v^2}$) of their volumes.

If now we have a certain number of crystals growing in a liquid metal that is being cooled from the outside, it may be that heat is removed in cooling faster than it is liberated by crystallization, and the temperature of the whole system falls. Smaller chance aggregates of atoms can then survive and grow, furnishing more area on which to deposit solid metal. Heat is evolved faster for this reason and also because the original crystals are growing larger. As the process continues, finally crystallization furnishes heat as rapidly as it is lost, and the temperature quits falling. If it has dropped below the orthodox melting point, it may even rise again to that temperature; but it will not rise higher, for if it did, even large solid masses could no longer remain solid, and the crystals would remelt.

Cooling slowly permits a very few crystals to give up heat fast enough to prevent supercooling and results also in large crystals; and the opposite results from quick cooling. Supercooling may also cause the formation of a metastable state, a matter of enormous technical importance whose further discussion does not fit in at this point. For the present, let the reader remember that supercooling has much to do with metastability.

Arrhenius' equation suggests that if k be the linear crystallization velocity at temperature T (abs) then

$$\ln k = e^{(-E/RT)} + I. \quad (1)$$

Here I is an experimental constant and E is the energy required to present a molecule of the substance to the surface of a crystal in a position favorable for its attachment. For monatomic metals, E should be small, and k changes but little with temperature.

Electric Furnaces and Heat Losses in Steady State

TO MELT SOMETHING heat must be applied. The source of any earthly energy now in use is that which in the present or the past reached the planet from the sun. Probably the ultimate source of this power is atomic disintegration in the sun, by which matter is converted directly into energy in accordance with the Einstein equation mentioned in an earlier chapter. On a small scale, solar radiation may be applied directly, as did Priestley when he made oxygen by heating the red oxide of mercury with a burning glass, that is, by concentrating radiation on his material with a convex lens.

Solar Origin of Energy

Our fuels are the products of chemical changes in what was once living matter. In plants, carbon dioxide is converted into combustible carbon compounds by means of the light and heat of the sun. This cannot be done in animals, but they get the energy by eating plants. When,

geologic ages later, we burn the coal or oil resulting from the metamorphosis of these living creatures, or years later burn the wood or charcoal of a tree, we merely recover some of the radiant energy that fell upon the plant years, centuries, or thousands of millenniums earlier.

If we generate power by harnessing a waterfall, we merely recover some energy absorbed by water evaporating from the ocean. The resulting vapor rose and was transported as a cloud to hills or mountains where, falling as rain or snow, it became available at a level somewhat or greatly above that of the ocean surface. Our hydroelectric plants are merely devices for recovering a part of the resulting potential energy.

The use of electric energy in melting, or other heating, of metal is not only becoming practically the most convenient source of heat but also presents the simplest approach to a study of furnace conditions.

Electrical Energy

If a current flows through a conductor, which of necessity must have electrical resistance, then Ohm's law, known to every high-school boy, says that

$$I = \frac{E}{R}. \quad (1)$$

Here I is the rate of flow of current (amperes), E is the fall of potential through the conductor (volts), and R is the resistance (ohms). The same proverbial high-school boy also knows that the power required to maintain these conditions is

$$W = EI, \quad (2)$$

where W (watts) is power or the rate of doing work. It is generally convenient to combine Equations (1) and (2) so as to eliminate either E or I and include R , which is ordinarily known for a given conductor, and so correlate W

with either E or I , which may be varied if the rate of heat input is varied. Thus we have

$$W = I^2 R \quad (3)$$

or

$$W = \frac{E^2}{R} \quad (4)$$

Since W is a rate of doing work, Wt (power multiplied by the time during which W is used) is work or energy, but the calorie or any other heat unit is also a measure of energy, and from the law of conservation of energy there must be then a proportionality between calories and watt-hours. Actually by experiment, direct or indirect, it can be shown that

$$1 \text{ kwhr} = 860,000 \text{ g-cal.} \quad (5)$$

$$1 \text{ kwhr} = 860 \text{ kg-cal.} \quad (6)$$

$$1 \text{ whr} = 0.860 \text{ kg-cal.} \quad (7)$$

$$1 \text{ whr} = 860 \text{ g-cal.} \quad (8)$$

$$1 \text{ coulomb} = 1 \text{ amp-sec (by definition).}$$

$$1 \text{ volt-coulomb} = 1 \text{ watt-sec.} \\ = 0.239 + \text{ g-cal.} \quad (9)$$

Let the reader not forget that if the current within a furnace is regulated by including an external variable resistance, that controller also dissipates heat. If the resistance of the furnace is R_1 and there is no external resistance, and if the applied voltage is always E , the energy is all consumed in the furnace and is equal to E^2/R_1 . If now, without a change of voltage, an external resistance R_2 is inserted, the current flowing becomes

$$I_2 = \frac{E}{R_1 + R_2}$$

The total power becomes $\frac{E^2}{R_1 + R_2}$, but the voltage drop in the furnace will be $\frac{R_1 E}{R_1 + R_2}$. Its power consumption is

then $\frac{R_1}{(R_1 + R_2)^2} E^2$, and the electrical efficiency of the set is

$$\frac{R_1}{(R_1 + R_2)^2} E^2 \div \frac{E^2}{R_1 + R_2} = \frac{R_1}{R_1 + R_2}. \quad (10)$$

This efficiency thus falls rapidly as the external resistance rises. To avoid this inefficiency, it is customary to control not the current with a constant voltage but the voltage itself. Since commercial equipment of any size is always operated on alternating current, this control is accomplished by the use of transformers having a number of taps in their secondary coils by means of which a selection of voltages may be obtained.

If more and more heat were liberated in an enclosure from which none could escape, evidently the temperature would rise indefinitely. Sooner or later the structure or its contents would be melted and vaporized. A simple example of the latter is found in the electric arc, whose temperature rises to the sublimation temperature of carbon, where the solid vaporizes without passing through the liquid stage. After that temperature is reached, the arc gets no hotter, the electric input being converted into the latent heat of vaporization of carbon, and the gas escaping from the region of the arc and taking heat, both sensible and latent, with it.

Let the reader be reminded that there is nothing very strange about a solid's passing directly into a gas. It happens with dry ice (solid CO_2), with iodine, with HgCl_2 , and with many other substances. There is nothing in the equations for the changes of free energy of a substance with temperature which requires that as the temperature rises, first the solid state, then the liquid state, and finally the gaseous state should have the lowest free energy. The gaseous state may have a lower free energy than the solid at temperatures at which the liquid still has a higher free

energy than the gas. It cannot happen that the free energy of the gaseous state is higher than that of the liquid at any temperature higher than one at which the opposite relation existed. We cannot have the order solid, gas, liquid with increasing temperature.

If the reader has not forgotten that the free energy of a gas changes much more rapidly with pressure than that of either a liquid or a solid, he will at once have seen that the relative positions of the points at which the free energy curves of the gas intersect those of the solid and liquid will be readily displaced by changes of pressure, while the other intersection of the other two is not much altered. Therefore, whether sublimation or melting occurs depends enormously on the pressure. Low pressure favors the former, high pressure the latter.

Returning now to the furnace in which we were constantly accumulating heat units when this digression began, we find that it has not yet melted completely because we could not completely prevent the flow of heat through the walls. These got hotter and hotter until the outer surface reached a temperature at which it would give off heat as fast as it was being generated. This will always happen unless the structure fails first.

Steady State of Heat Transfer through Furnace Walls

Heat leaves the outer surface, in practical cases, mainly by *convection*. That is, the adjacent air is heated, first by conduction, but then it immediately becomes lighter and rises, taking away heat in proportion to the amount of air passing by a given surface. The principle remains the same if the exterior is water cooled.

The mathematical expressions for the cooling of a furnace wall by convection have eluded the experts, because of the complexity of the conditions. At least they would have to include the effects of temperature differences on the rate of the convection currents, the effect of this velocity on the rate of heat transfer, and the effect of character of surface

and of temperature changes on the physical properties of the cooling medium.

Textbooks commonly contain a graph indicating the amount of heat lost per unit area from furnace walls to air at ordinary room temperature as a function of the difference in temperature between the wall and air. These graphs are equivalent to saying that the heat loss from the wall per square centimeter per second is

$$\frac{\Delta H}{\Delta t} = 0.74(\Delta\theta) + 0.018(\Delta\theta)^2, \quad (11)$$

where $\Delta\theta$ is the temperature difference between wall and ambient air in centigrade degrees.

Equation (11) is valid only for values of $\Delta\theta$ below 250°C . At greater temperature differences the heat loss becomes decidedly greater than that calculated from Equation (11), perhaps because of a contribution by radiation. More of heat transfer by radiation will be found in Chapter 15.

Having arrived at the concept of a *steady state* in which neither face of the furnace wall, nor any point in the wall, is changing temperature, we have before us a flat slab (chosen for simplicity) of unchanging temperature throughout, through which heat is flowing. Through every unit of area, parallel to the furnace wall, the same amount of heat flows, no matter where in the wall's thickness the area is chosen, and hence no matter what the temperature. If more heat flowed in one place than in another, the material between would gain or lose heat units, and hence unchanging temperature and the steady state would not exist.

Fourier's law states that the rate of heat flow through a given area is proportional to the thermal gradient at that surface. The constant of proportionality is called the thermal conductivity of the material and varies with different substances and also usually with temperature. The differential equation for heat flow is, then,

$$\frac{dH}{dt} = -\kappa \frac{d\theta}{dx}. \quad (12)$$

Here H is quantity of heat, t is time, θ is temperature, and x is distance in the direction of heat flow.

If κ can be considered constant throughout the temperature range existing in the wall, then $d\theta/dx$ is constant and is equal to $\Delta\theta/x$, where $\Delta\theta$ is the difference in temperature existing between the two faces of the wall, and

$$\frac{dH}{dt} = \kappa \frac{\Delta\theta}{x}. \quad (13)$$

When this equation is integrated it becomes

$$H = -\kappa t \frac{\Delta\theta}{x}. \quad (14)$$

That is, the amount of heat flowing (through a unit area of a flat wall) is the product of the conductivity, the time, the difference between the temperatures of the inner and outer faces of the wall, and the reciprocal of the wall's thickness.

Since dH/dt is the heat input per unit area of wall and is presumably known, $\Delta\theta/x$ and hence $\Delta\theta$ are determined, and the inner face of the wall has a temperature determined by the rate of heat input, the wall thickness and its conductivity, and the rate at which the wall loses heat to the air.

Since in any event dH/dt is the same throughout the walls, it follows that $\kappa(d\theta/dx)$ is also constant, and that the gradient $d\theta/dx$ varies inversely as the conductivity, whose relation to temperature may be experimentally known.

Regardless of the material or thickness of the furnace lining, Equation (11) fixes the rate per unit of area of exposed wall at which heat can be generated in a furnace for a given outside temperature or vice versa.

The inside temperature will depend upon the heat conductivity of the wall, as determined from Equation (14).

Calling the temperature difference between the inner and outer faces of the wall $\Delta\theta_1$, and that between the outer surface and the ambient atmosphere $\Delta\theta_2$, then for the steady state

$$\kappa \frac{\Delta\theta_1}{x} = 0.74(\Delta\theta_2) + 0.018(\Delta\theta_2)^2. \quad (15)$$

From this one may calculate either x , the appropriate wall thickness for a given value of $\Delta\theta_1$, or the drop of temperature that will take place through a wall of given thickness, all of course for a given conductivity κ and for a given external wall temperature.

Hence Equation (15) can be written

$$\Delta\theta_1 = \frac{x}{\kappa} [0.74(\Delta\theta_2) + 0.018(\Delta\theta_2)^2], \quad (16)$$

which is independent of any particular rate of heat transfer, provided only that it yields a value of $\Delta\theta_2$ below 250°C . It is plain that for a given thickness and material of wall there is a definite relation, in the steady state, between inside and outside wall temperatures.

If the wall thickness is great enough or the conductivity low enough (that is, if x/κ is large enough), then $\Delta\theta_1$ will become so great that the inside surface of the wall will melt off, thus reducing x and hence $\Delta\theta_1$. The process will continue until another sort of steady state is reached at which the inner wall face is just at the melting point. This condition is often found in practice.

When the heat is the result of combustion involving the escape of flue gases, the problem involves additional considerations, to be taken up in what follows immediately. Also, if heating is not continued long enough to produce the steady state, the problems are much more complex.

If $\Delta\theta_0$ is the difference between the refractory's melting point and the room temperature, then

$$\Delta\theta_0 = \Delta\theta_1 + \Delta\theta_2$$

and

$$\Delta\theta_0 - \Delta\theta_2 = \frac{x}{\kappa} [0.74(\Delta\theta_2) + 0.018(\Delta\theta_2)^2]. \quad (17)$$

For known values of $\Delta\theta_0$, $\Delta\theta_2$, and κ , the maximum thick-

ness of a wall that will maintain itself without melting can be calculated by solving Equation (17) for x .

The expression in the brackets in Equation (17) and $\Delta\theta_2$ are related to the rate of heat input per second per unit area of furnace wall $\Delta H/\Delta t$ through Equation (11). Making the proper substitutions, we have

$$\Delta\theta_0 = \frac{x}{\kappa} \frac{dH}{dt} + \sqrt{55.6(\Delta H/dT) + 400} - 20, \quad (18)$$

which is an expression permitting a calculation of the maximum value of wall thickness x for a given rate of heat input and a given conductivity and melting point of refractory. The expression fails for conditions giving values of $\Delta\theta_2$ above 250°C .

CHAPTER 10

Carbon Combustion

THE TEMPERATURE PROBLEM in a fuel-fired furnace differs from that in an electric furnace in that while in the latter the temperature will increase indefinitely with rate of heat input—of course within the limit that destroys the furnace—in the former the combustion process itself sets a limit to the temperature that can be reached.

The heat of combustion of the fuel is first transferred to the products of combustion (usually gaseous) and from there to the furnace and charge. The products must leave the furnace to make room for more fuel and air and in so doing they unavoidably carry out heat units equivalent to the product of their mass, specific heat, and temperature. A steady state would be reached if the completely insulating furnace structure had the temperature that the products of combustion would have if all the heat of reaction (combustion) were transferred to the resulting products. These conditions are, of course, never attained, but they serve to explain the principles. Then all the heat liberated flows out of the stack end of the furnace.

Flame Temperature

Since there is always a loss of heat through the furnace walls, the maximum realized temperature is less than the theoretical maximum by the amount of this heat loss through the wall (per unit of fuel); this loss leaves less heat for transmission to the products of combustion.

Here seems to be the proper place to introduce consideration of the chemistry of combustion, which is also a suitable subject for acquainting us with the *mass law* applicable to all chemical reactions in what may be called mobile systems. Mobile systems are those which permit sufficiently rapid molecular motion to prevent equilibrium from being retarded by lack of opportunity for reaction products to diffuse.

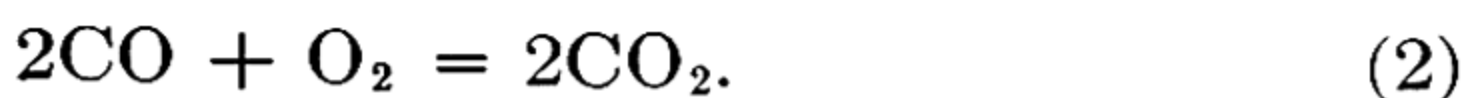
The most common fuel is carbon. In the cupola, the source of heat is nearly always the burning of this element in the form of coke. Furnaces burning bituminous coal, oil, or gas use also the heat of combustion of the hydrogen of these fuels, and no other elements are especially important as sources of energy, although in various refining processes the heat of combustion of other elements may need consideration.

To say that carbon burns with oxygen to form CO_2 , yielding 7857 cal/g C or 94,285 cal/g atom C, until one or the other element is used up, is a very unjustifiable oversimplification. It may also burn to form CO, yielding 2202 cal/g C or 26,428 cal/g atom C. Before any conclusion can be reached as to the amount of heat liberated and the temperature of the resulting gases, we must know what the composition of the resulting gases is. This depends upon the temperature and upon whether C or O_2 is present in excess.

If carbon is in excess, as in the upper part of a cupola or of a gas producer, it is necessary to consider the reaction



If O_2 is in excess, as for example near the tuyères of a cupola, the reaction is



Both cannot be applicable at the same time, strictly speaking, although opposite the tuyères of a cupola, for example, the gases pass so rapidly over coke that the equilibrium is reached with excess O_2 and not with C, because of lack of time for the gases to react with solid carbon; that is, the mobility is insufficient.

Mass Law

Such a reaction as indicated in Equation (1) or (2) will move either way, according to the relative amounts of the reactants and products available, that is, according to their partial pressure. The forgetful may be reminded that the partial pressure of a constituent in a gas is the product of the total pressure of the gas and the volume concentration of that constituent. The reaction could proceed in either direction, but it comes to rest (equilibrium) when it proceeds equally fast in both directions. This is the law of mass action enunciated long ago by Guldberg and Waage.

To make it easier to follow the more immediate subject, we leave out here the very interesting considerations that affect the rate at which a reaction goes on as the reactants are used up.

The conditions for equilibrium can be defined by an equilibrium constant called, like so many other constants, K .

At a given temperature this constant K has a specific value, regardless of the absolute values of the partial pressures. It represents a relation of partial pressures, arrived at from probability considerations, that cause the reaction rates in opposite directions to be equal.

For Equation (1)

$$K = \frac{P_{CO}^2}{P_{CO_2}}, \quad (3)$$

and for Equation (2)

$$K = \frac{P_{\text{CO}_2}^2}{P_{\text{CO}}^2 P_{\text{O}_2}} \quad (4)$$

The expression for K is constructed as follows. The numerator is the product of the partial pressures of the constituents to the right of the equality sign in Equation (1) or (2), each pressure raised to the power corresponding to the number of molecules involved. The denominator is a similar product derived from the left side of the equation.

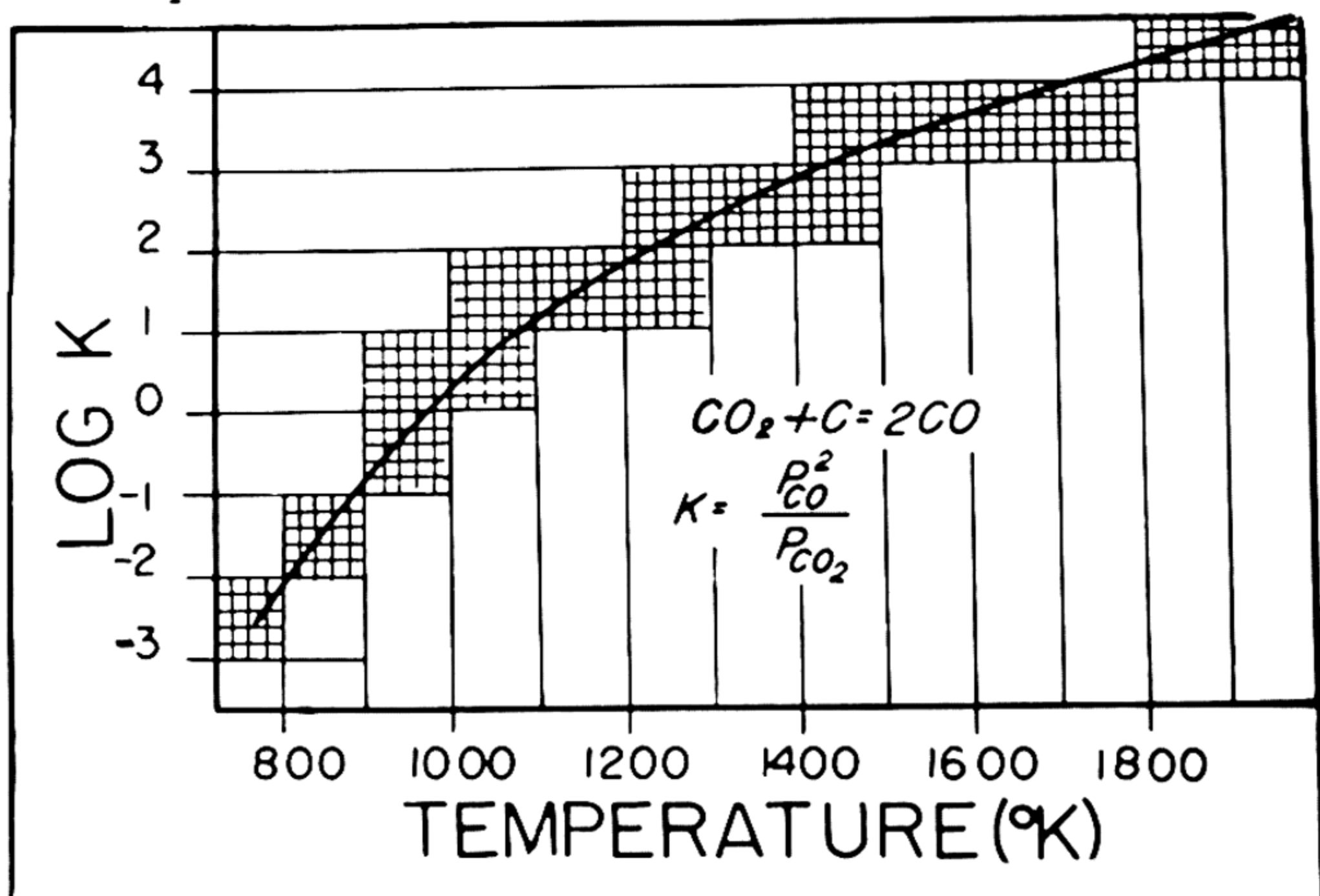


FIG. 10-1. Equilibrium Constant of Reaction $\text{CO}_2 + \text{C} = 2\text{CO}$. (Calculated from data of Lewis and Randall and Haslam and Russell.)

The partial pressure of a solid present in excess is not considered, for it is present throughout the reaction and would appear equally in the numerator and denominator and so cancel out. The partial pressure (vapor pressure) of such an excess phase does not depend upon the *amount* of solid present.

The value of K for either equation is known experimentally with considerable accuracy over a quite wide

range of temperature and is shown graphically in Figs. 10-1 and 10-2. One can calculate, therefore, from Equation (3) the relative amount of CO and CO₂ in the presence of an excess of carbon at any temperature and for any sum of the partial pressures of the two gases. Similarly, one can calculate from Equation (4) the partial pressure of oxygen required to maintain any given ratio of $P_{\text{CO}_2}/P_{\text{CO}}$, since from Equation (4)

$$P_{\text{O}_2} = \frac{1}{K} \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right)^2. \quad (5)$$

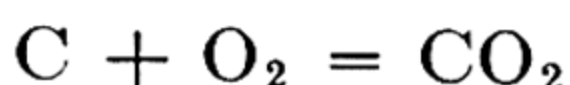
Since, also irrespective of total pressure,

$$\frac{v_{\text{CO}_2}}{v_{\text{CO}}} = \frac{P_{\text{CO}_2}}{P_{\text{CO}}}, \quad (6)$$

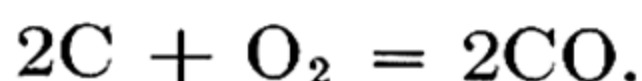
where v is the volume concentration of the gas indicated by the subscript, therefore

$$P_{\text{O}_2} = \frac{1}{K} \left(\frac{v_{\text{CO}_2}}{v_{\text{CO}}} \right)^2. \quad (7)$$

To calculate the conditions that will produce a flue gas of a given composition, consider first the two reactions



and



One volume of oxygen forms one volume of CO₂ or 2 of CO (since the gram molecule of all perfect gases has the same volume, and at high temperatures CO₂ will at least approximate a perfect gas).

The volume of oxygen required to burn carbon to a predetermined mixture of CO₂ and CO, neglecting the necessary excess of O₂ represented by Equation (7), is found then (using v for volume fractions of the several gases and assuming a total gas pressure of 1 atmosphere) to be

$$v_{\text{O}_2} = v_{\text{CO}_2} + \frac{1}{2}v_{\text{CO}}. \quad (8)$$

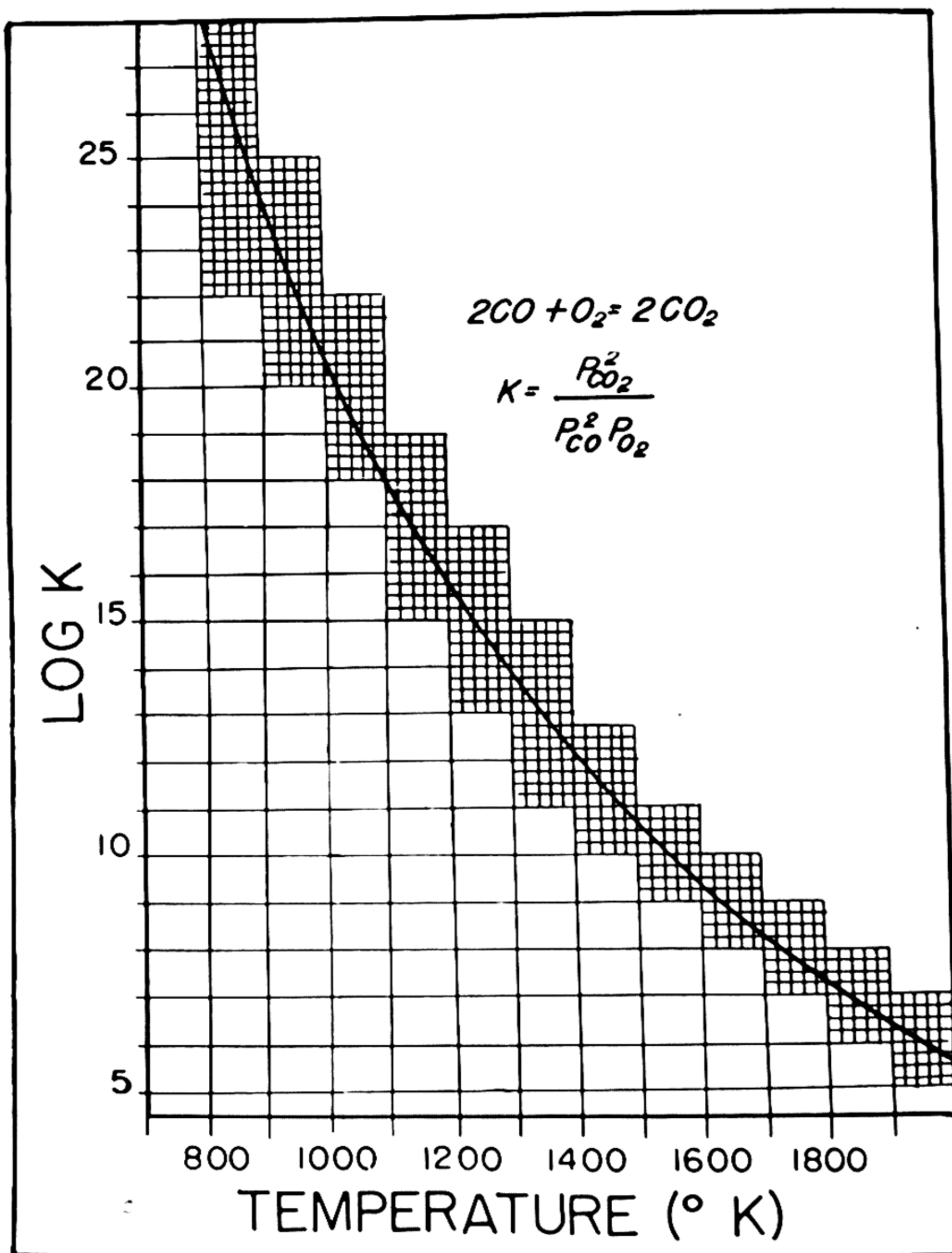


FIG. 10-2. Equilibrium Constant of Reaction $2\text{CO} + \text{O}_2 = 2\text{CO}_2$. (Calculated from data of Lewis and Randall and Haslam and Russell.)

Since ordinarily we burn things in air which, in round figures, contains 1 volume of O_2 for 4 volumes of N_2 ,

$$v_{N_2} = 4v_{CO_2} + 2v_{CO}. \quad (9)$$

If, as usual, the pressure is 1 atmosphere, then from Equation (7)

$$P_{O_2} = v_{O_2} = \frac{1}{K} \left(\frac{v_{CO_2}}{v_{CO}} \right)^2, \quad (10)$$

and with this will go a volume of nitrogen,

$$v_{N_2} = \frac{4}{K} \left(\frac{P_{CO_2}}{P_{CO}} \right)^2. \quad (11)$$

The total volume of the gas, equal to unity, is then

$$v_{CO_2} + \frac{1}{2}v_{CO} + 4v_{CO_2} + 2v_{CO} + \frac{5}{K} \left(\frac{N_{CO_2}}{v_{CO}} \right)^2 = 1.$$

Having decided in advance what ratio of CO_2 to CO we want and calling that ratio α , we proceed

$$v_{CO_2} = \alpha v_{CO};$$

$$\alpha v_{CO} + \frac{1}{2}v_{CO} + 4\alpha v_{CO} + 2v_{CO} + \frac{5\alpha^2}{K} = 1,$$

$$5\alpha^2 v_{CO} + 2.5v_{CO} + \frac{5\alpha^2}{K} = 1,$$

$$(1 - 2\alpha)v_{CO} = 0.4 - \frac{2\alpha^2}{K}.$$

From Equation (10),

$$v_{O_2} = \frac{\alpha^2}{K},$$

$$(1 - 2\alpha)v_{CO_2} = \alpha \left(0.4 - \frac{2\alpha^2}{K} \right).$$

(12)

We are still confronted with a selection of K , which is a function of partial pressures, not of volume concentration. It is, however, immaterial for the purpose of calculating K in the presence of inert N_2 , whether we calculate partial pressures from the volume concentrations in the 4-com-

ponent gas (N_2 , CO_2 , CO , and O_2) and a total pressure of unity or from the *relative* concentrations of the reacting gases and their aggregate partial pressures ($1 - v_{\text{N}_2}$).

Our calculation applies, of course, only to one particular temperature if we choose a particular value of K , but we can apply it to any temperature if we have a table of K for various temperatures.

Computation of Flame Temperature

The purpose of all this algebraic effort to compute the composition of a flue gas is to arrive at the heat content of such a product at any given temperature. From their formulas, CO_2 and CO , it is evident that burning 1 gram atom of carbon to either gas produces a gram molecule of gas. This will prove very convenient, since the specific heat of any diatomic gas, except H_2 , is the same per gram molecule.

The heat of combustion of 1 gram atom (12 grams) of carbon to a mixture of CO_2 and CO in which the volumes are in the ratio α , as just discussed, is

$$\frac{94,285\alpha + 26,428}{\alpha + 1}. \quad (13)$$

To know the calorific effect, or theoretical flame temperature, we must divide this value by the mean specific heat of the products of combustion. Unfortunately, this number is not constant, even for a single gas, but increases with the temperature. Remember also the statement that K is a function of temperature.

It is, however, possible to compute the compositions, choosing values of K appropriate to various temperatures and then computing the heat content at the same temperatures, remembering that for 1 gram atom of carbon, at atmospheric pressure,

$$v_{\text{CO}_2} + v_{\text{CO}} = [(\alpha + 1)v_{\text{CO}}] = 1 \text{ (g mol)}. \quad (14)$$

This permits the calculation of the number of gram

molecules of each gas in the products of combustion of 1 gram atom of carbon at a given temperature, and hence the heat content at that temperature.

Making this calculation for a series of temperatures permits one to plot a curve of heat content versus temperature. The temperature at which this heat content is the heat of combustion calculated from Equation (13) is the flue gas temperature, in the absence of any heat losses whatever. This problem is somewhat simpler than the practical one of what is the highest temperature that can be reached by burning carbon in air. So far, we have assumed a given ratio of CO_2 and CO . The new problem involves the question of using just that amount of air which will supply the amount of oxygen excess to produce the CO_2 - CO ratio that will give the highest temperature. The only simple solution is again a graphic one and is illustrated in Fig. 10-3.

The abscissas (horizontal) represent the fraction of CO_2 or CO in the gas mixture. Measuring vertically at the CO_2 end of the diagram the heat of combustion (per gram molecule) of carbon to CO_2 , and at the CO end its heat of combustion to CO , and joining the two points, gives a line showing the heat given off with changing gas composition.

Setting off, on the two ordinates $\text{CO}_2 = 1$ and $\text{CO} = 1$, the sum of the heat contents of a gram molecule of each gas and of the nitrogen that accompanies its oxygen (4 gram molecules per gram molecule of CO_2 or 2 per gram molecule of CO) and joining corresponding points gives a series of straight lines, each for a different temperature, representing the heat content of the CO , CO_2 , and accompanying N_2 corresponding to the combustion of 1 gram molecule of carbon.

But we must take account also of the excess of O_2 and its accompanying N_2 to produce, at the higher temperatures, the higher ratios of CO_2 to CO . At atmospheric pressure, the volume fraction of O_2 corresponding (at a given temperature, which determines K) to a given ratio of CO_2/CO ,

which is α , is given by Equation (12), and the corresponding volume of air is obviously 5 times that amount. This leaves a remainder as the volume of the products of combustion of carbon in air of $1 - (5\alpha/\sqrt{K})$. From Equation (12) we know the volume fraction of CO, and since the CO

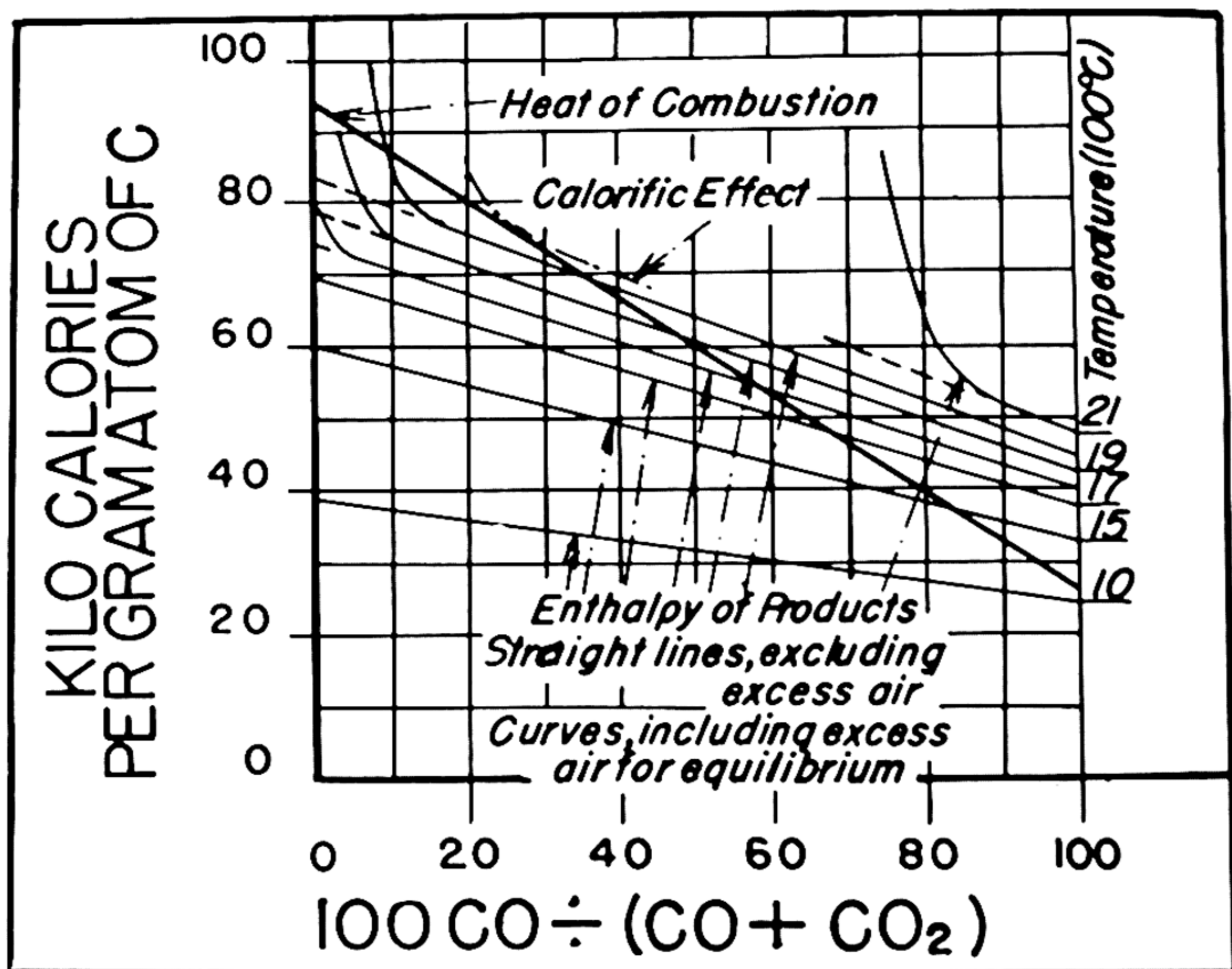


FIG. 10-3. Calorific Effect of Carbon Burned in Excess Air.

derived from 1 gram molecule of carbon is $1/(1 + \alpha)$ gram molecules, it is easy to calculate that the number of gram molecules of air ($O_2 + 4N_2$) is

$$\frac{1}{1 + \alpha} \left[\frac{5\alpha}{\sqrt{K}} \div \left(\frac{0.4}{1 + 2\alpha} - \frac{2\alpha}{(1 + 2\alpha)\sqrt{K}} \right) \right] = \frac{1}{1 + \alpha} \frac{5\alpha(1 + 2\alpha)}{0.4\sqrt{K} - 2\alpha}. \quad (15)$$

The value of this expression for any given temperature, and hence for K , can be calculated for any desired value of

α , that is, the CO and CO₂ content. Multiplied by the mean specific heat of air between zero and the chosen temperature, this gives an amount to be added to the heat content previously represented by a straight line for the given temperature.

A series of isotherms result, turning sharply upward with increasing CO₂ content. The lower isotherms are intersected twice by the heat of combustion line, the upper not at all. There is one isotherm and one only to which the locus of the heat of combustion is tangent. Its temperature is the calorific effect of carbon.

If we were interested only in that temperature as an isolated fact, paper and ink might be saved by making the calculation privately and merely recording the result here. The subject is developed in such detail to give the reader a quantitative understanding of the combustion of carbon and also as a basis for the discussion of hydrocarbon fuels that follows immediately.

The problem of a maximum temperature in a furnace losing heat through the walls can be approached as follows. From Equation (13) of Chapter 9 the heat loss per unit of time per unit area of wall is known for a given inside and outside wall temperature and wall thickness. If one knows the number of gram atoms of carbon burned per unit of time per unit area of wall, it can be determined that the corresponding heat loss must be that furnished by a gram atom of carbon together with that corresponding to the sensible heat content of the gases represented by the isotherms of Fig. 10-3. The effect is to move each isotherm upward by that distance representing the heat loss through the walls per gram atom of carbon at that particular temperature.

The calculations of this chapter were based on fuel and air at 0°C (273°K). If their temperature is higher, the isotherms are moved downward by an amount representing the sensible heat of the coke and air above that at 0°C.

Carbon and Hydrogen Combustion

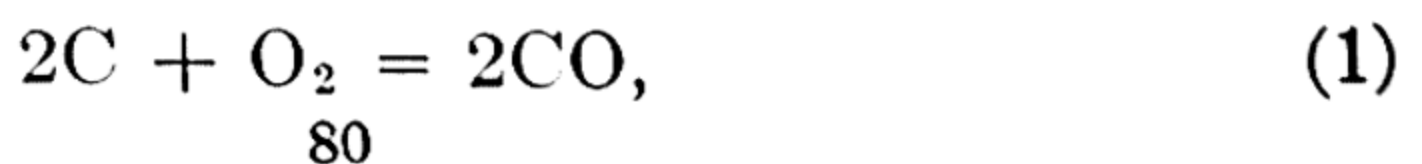
THERE ARE DIFFICULTIES, when burning a solid like carbon (coke), in maintaining continuously any definite ratio of carbon to oxygen. Fuel beds develop passages through which air passes without reacting with carbon, and if the oxygen supply is such as not to form CO, which might later react with such surplus air, an excess of oxygen over the most efficient ratio is inevitable.

It is not uncommon to consider that, when burning solid fuel in a grate, about twice the theoretical amount of oxygen required to form CO₂ is necessary to avoid CO in the flue gas.

In foundry furnaces gaseous fuels are preferred in many operations. These fall into four classes: carbon monoxide in producer gas; mixtures of carbon monoxide and hydrogen in water gas; and gaseous hydrocarbons, either the paraffins C_nH_{2n+2} of natural gas, largely methane, CH₄, or the olefines C_nH_{2n} of coal gas, principally ethylene, C₂H₄. These and their combustion may be considered in order.

Producer Gas

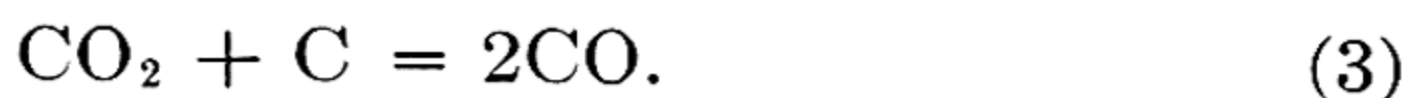
Producer gas is made in principle by the reaction



which is, however, always accompanied by the reaction



What composition actually results is determined by the equilibrium conditions of the reaction



The CO_2 is originally the product of reaction (2) so that the combined reactions (2) and (3) result in reaction (1).

Now by the principles discussed in Fig. 10-2 (in the preceding chapter) from reaction (3) we may derive an equilibrium constant

$$K = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}}. \quad (4)$$

This K , which must not be confused with other equilibrium constants similarly designated for other reactions, is as usual dependent upon temperature.

Since we are going to operate at near atmospheric pressure, we can similarly say

$$K = \frac{v_{\text{CO}}^2}{v_{\text{CO}_2}} \quad (5)$$

and

$$v_{\text{CO}} = \sqrt{K v_{\text{CO}_2}}, \quad (6)$$

since the volume fraction of a constituent of a gaseous mixture is its partial pressure P divided by the total pressure.

The volume of oxygen from which the mixture of CO and CO_2 in unit volume of flue gas came was $v_{\text{CO}_2} + \frac{1}{2}v_{\text{CO}}$, since one volume of O_2 produces one volume of CO_2 but two volumes of CO from reactions (1) and (2). This O_2 was accompanied by, approximately, four times its volume of N_2 , that is, $4v_{\text{CO}_2} + 2v_{\text{CO}}$, and hence

$$v_{\text{CO}} + v_{\text{CO}_2} + 4v_{\text{CO}_2} + 2v_{\text{CO}} = 1,$$

or

$$5v_{\text{CO}_2} + 3v_{\text{CO}} = 1. \quad (7)$$

Substituting for v_{CO_2} its value from Equation (6), we have

$$5 \frac{v_{\text{CO}}^2}{K} + 3v_{\text{CO}} = 1. \quad (8)$$

The value of K increases with temperature until at about 1000°C the value of v_{CO_2} , that is, $5 \frac{v_{\text{CO}}^2}{K}$, becomes negligible and $v_{\text{CO}} = 0.33$.

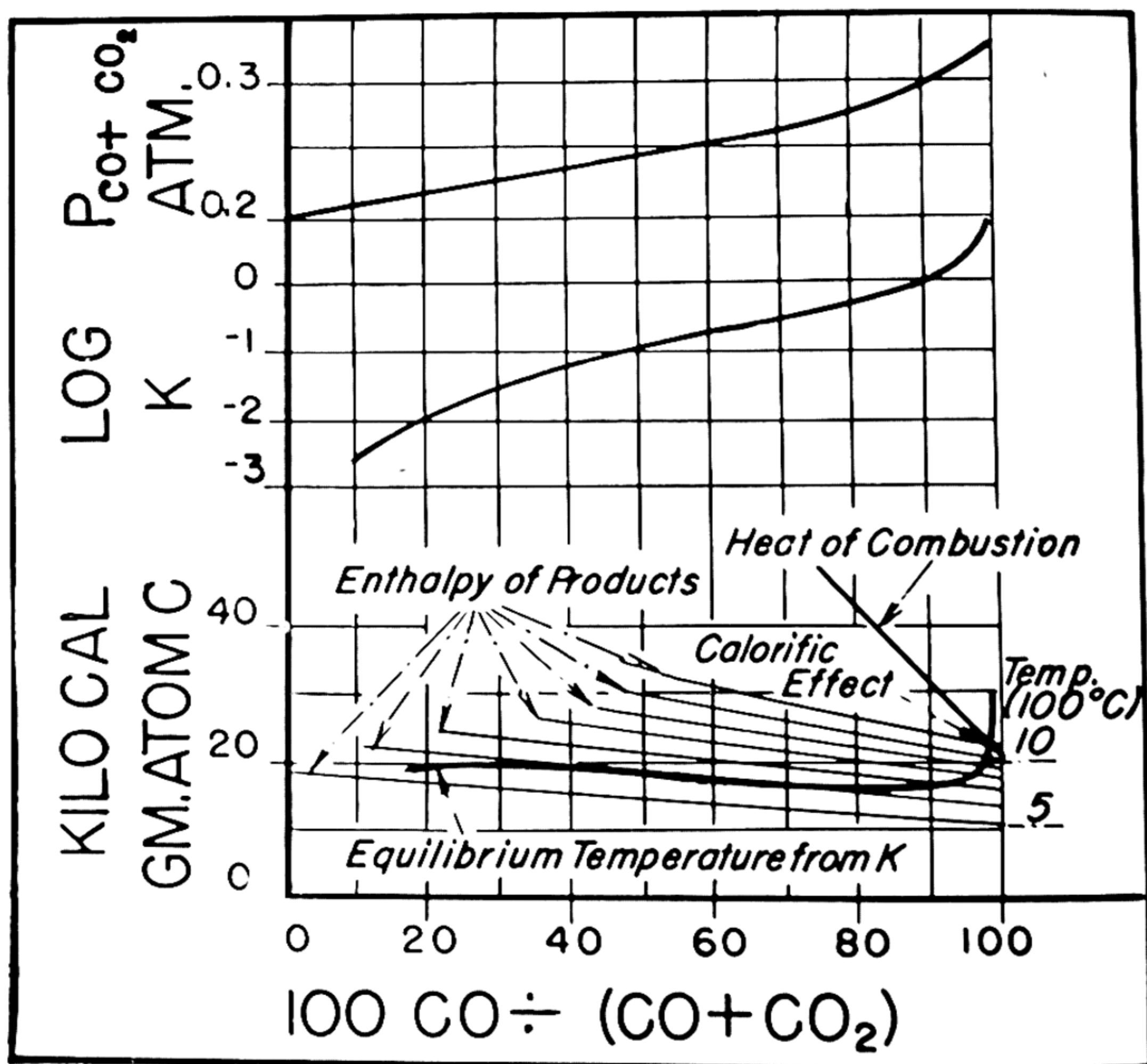


FIG. 11-1. Calorific Effect of Carbon Burned in Insufficient Air.

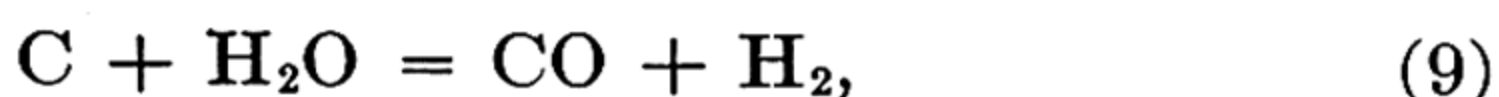
Fig. 10-1 (in the preceding chapter) shows that the temperature developed by burning carbon to pure carbon monoxide in air may reach 1000°C . In contact with C there is a fixed CO-CO₂ ratio for each temperature and

pressure of $\text{CO} + \text{CO}_2$. Starting with air, the partial pressure varies with the $\text{CO}-\text{CO}_2$ ratio. Fig. 11-1 is similar to Fig. 10-1 (Chapter 10); the curved line represents equilibrium composition for combustion with air. Evidently the calorific effect of C to CO is sufficient to keep CO practically pure. A fall of temperature in the producer results in the formation of CO_2 and impairs the efficiency of the gas as a fuel.

If producer gas is piped any distance, its sensible heat, arising from the combustion of carbon to carbon monoxide, is largely or completely lost. In the latter case, Fig. 10-1 (in the preceding chapter) would be modified by shifting the line of zero temperature upward until it passed through the heat of combustion of a gram atom of carbon to carbon monoxide. The corrections for excess of oxygen that manifest themselves only at higher temperatures would then disappear, for the combustion of CO to CO_2 would not yield a high enough temperature for a significant dissociation, and Fig. 10-1 would be converted to Fig. 11-2.

Water Gas

Blowing a producer with steam instead of with air produces water gas by the reaction



which results in a completely combustible gas uncontaminated with nitrogen. Fig. 11-2 shows the relation of the equilibrium constant to temperature.

Water gas has been used much more as a domestic fuel than in metallurgy. City gas supplies have been either entirely water gas or a mixture of water gas and coal gas. Its production and combustion present a convenient illustration for the equilibriums of C, H_2 , and O_2 .

In order for reaction (9) to proceed, the fuel bed must be initially hot enough for the reaction to go on at a usable rate. Since the heat of formation of CO is 26,428 cal/g mol

and that of water (steam) is 57,826 cal/g mol, it is plain that the heat of reaction (9) in which one gram molecule of steam disappears and one of CO appears is the difference between these two numbers, which is a negative number. The reaction still goes on, so that it must be accompanied

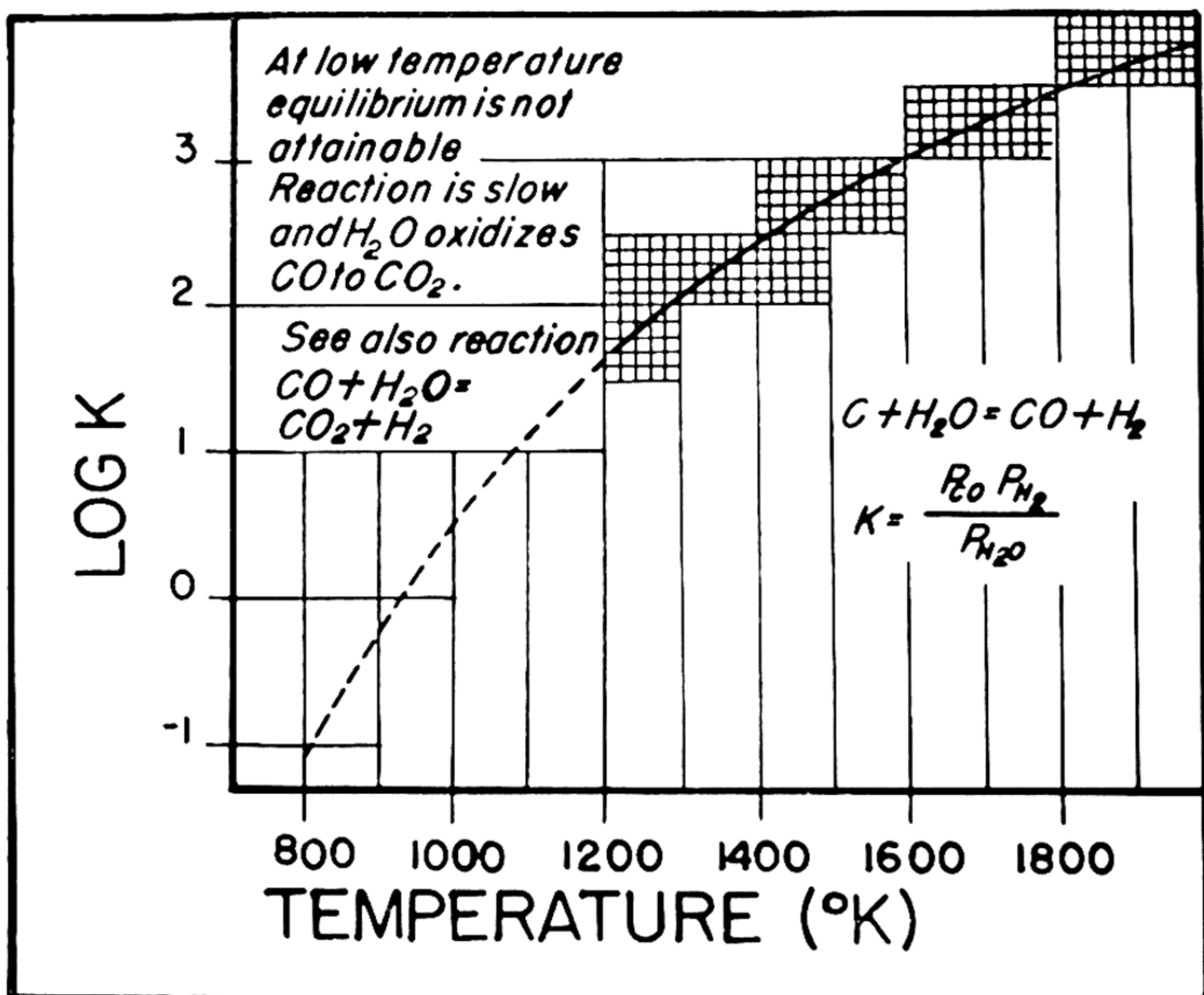


FIG. 11-2. Equilibrium Constant of C- H_2 - O_2 Equilibrium. (Calculated from data of Lewis and Randall and Haslam and Russell.)

by a decrease in free energy, even though it is endothermic, that is, accompanied by the absorption of heat. It is an excellent illustration of the fallacy that spontaneous reactions evolve heat.

The temperature of the fuel bed falls until it becomes too low to have the reaction proceed at a useful, or even a measurable, speed. It must then be restored by blowing with air, either mixing the resulting producer gas with the water gas or diverting it into any other distributing systems.

It is also possible to so proportion the simultaneous supply of steam and air that the temperature of the fuel bed is exactly maintained. Since the production of one gram molecule of CO from C and O₂ evolves 26,428 cal, and from C and H₂O absorbs 31,398 cal, and since the formation of a gram molecule of CO requires $\frac{1}{2}$ gram molecule of O₂ or 1 gram molecule of steam, it follows very simply that, measured at the same temperature, above the boiling point the volume of O₂ and of H₂O must be in the ratio

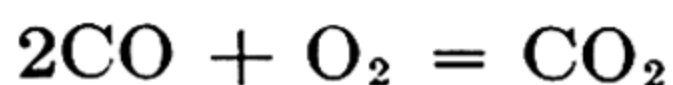
$$\frac{v_{\text{O}_2}}{v_{\text{H}_2}} = \frac{31,398}{26,428} = 1.19 \quad (10)$$

if the system is to neither gain nor lose heat. In practice a relatively larger amount of air must be used, not only because there are heat losses unavoidably present but also in order to obtain a working temperature high enough to maintain the reaction at a sufficient rate and efficiency.

Consideration of the possible incomplete dissociation of water or of the formation of CO₂ were here omitted as probably absent at the temperatures involved. This sort of simplification cannot be used when considering the combustion of water gas. Indeed, the principal purpose of talking about this gas at all is that it is the simplest example of a fuel containing both carbon and hydrogen.

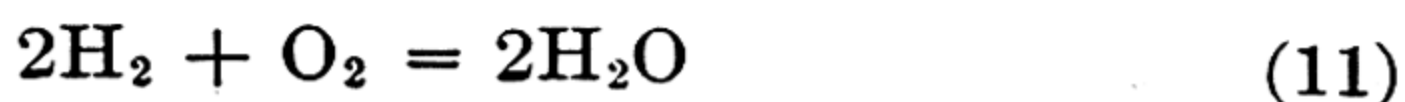
Carbon-Hydrogen-Oxygen Equilibria

In the preceding chapter we learned of an equilibrium constant K for the reaction



which for any given ratio of volume of CO and CO₂ lets us calculate the partial pressure of O₂ in the gas.

There is a similar though numerically different K for the reaction



such that

$$K = \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 P_{\text{O}_2}} \quad (12)$$

The relation of K to temperature is illustrated in Fig. 11-3.

Here again, as for the combustion of CO in the earlier chapter, a given ratio of H_2O and H_2 requires a given partial pressure of O_2 , regardless of the partial pressure of H_2O and H_2 .

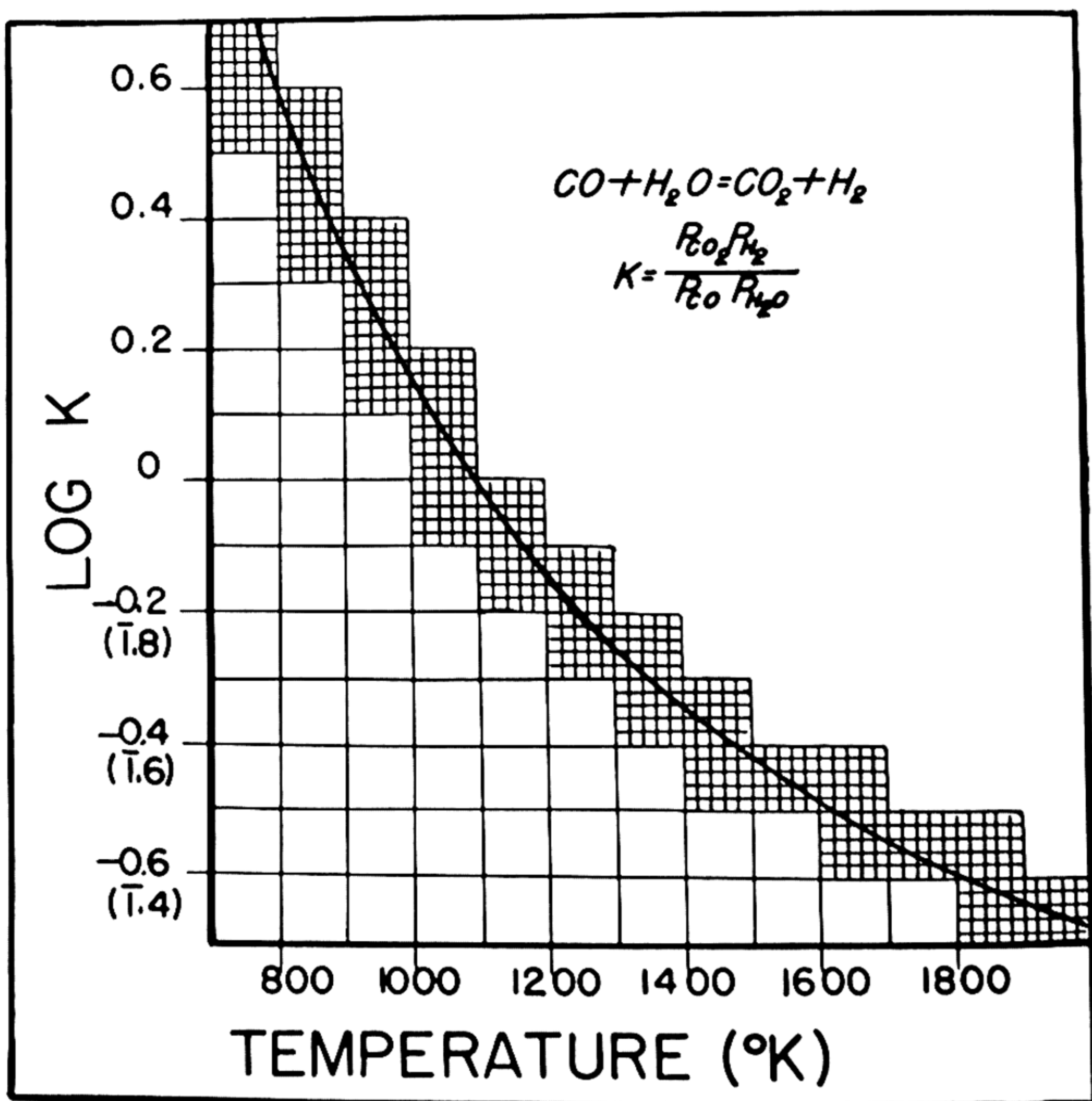


FIG. 11-3. Equilibrium Constant for Reaction $\text{CO} + \text{H}_2 = \text{CO}_2 + \text{H}_2$. (Calculated from data of Lewis and Randall and Haslam and Russell.)

One can make either of the following two equivalent statements:

$$P_{O_2} = \frac{1}{K} \frac{v_{H_2O}^2}{v_{H_2}^2}, \quad (13)$$

or

$$\frac{v_{H_2O}}{v_{H_2}} = \sqrt{KP_{O_2}}. \quad (14)$$

This assertion must not be misunderstood to mean that

$$\frac{v_{H_2O}}{v_{H_2}} = \frac{v_{CO_2}}{v_{CO}}.$$

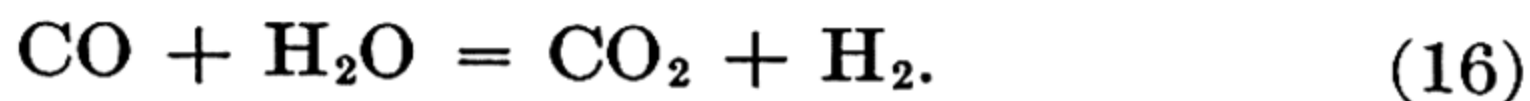
This would only be true if the K of the two reactions were the same, numerically, which it is not. Since in any given gas P_{O_2} has the same value, whether we consider it as part of the carbon reaction or of the hydrogen reaction, we can, however, say, by equating (13) and the similar equation for CO, Equation (10) (on page 75) of the preceding chapter,

$$\frac{1}{K_{H_2}} \frac{v_{H_2O}}{v_{H_2}} = \frac{1}{K_{CO}} \frac{v_{CO_2}}{v_{CO}}, \quad (15)$$

where K_{H_2} and K_{CO} are the two equilibrium constants for the combustion of H_2 and CO, respectively.

For the present we shall consider K_{H_2} and K_{CO} merely as experimental values known for every temperature, leaving for discussion in the next chapter how they vary with temperature. This will avoid distraction from the main theme of this chapter, which is the combustion of a fuel containing both C and H_2 .

Equation (15) could have been arrived at another way by considering the possible oxidation of CO by H_2O according to the reaction



Its equilibrium constant would be

$$K = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}. \quad (17)$$

Since at a given total pressure volumes are proportional to partial pressure, no matter what the *constant* total pressure may be, this can be rewritten as

$$K \frac{v_{\text{H}_2\text{O}}}{v_{\text{H}_2}} = \frac{v_{\text{CO}_2}}{v_{\text{CO}}}, \quad (18)$$

which is identical with Equation (15) if $K = K_{\text{CO}}/K_{\text{H}_2}$.

Let the reader make note, for other possible applications, of the interrelation of such equilibrium constants.

Calculation of Flame Temperature

The temperature of theoretical combustion of water gas can, in principle, be answered by a graphic solution similar to those previously outlined for carbon or hydrogen. In execution, however, the process is much more complicated. Starting with such a diagram as before, with the fraction or per cent of CO in the mixture of CO and CO₂, we can readily plot the heat content of the CO and CO₂ and of the nitrogen content corresponding to the oxygen that converted the CO into CO₂. To this we must add the heat content of the partially burned H₂, of which there is one gram molecule (all told) for every gram molecule of CO burned and unburned.

From Equation (18) we can determine the ratio of $v_{\text{H}_2\text{O}}/v_{\text{H}_2}$ for any chosen $v_{\text{CO}_2}/v_{\text{CO}}$ and temperature. If we remember that K is a function of temperature, we can then determine the heat content of the H₂, H₂O, and nitrogen in the products of combustion of hydrogen. Adding this to the heat content of the products of combustion of carbon permits the plotting of heat content of flue gas against the ratio of CO to CO₂ at a series of temperatures.

If the temperature is high enough to dissociate CO₂ (and also H₂O), we must add, as in the earlier problems, the heat content of the excess of air required to produce a given CO-CO₂ ratio. This would be found to be the same excess of air required for the H₂-H₂O ratio, for these equilibria

are interrelated as just explained. It is necessary to compute the excess of air from one of these ratios, but not from both, for the same excess is effective in controlling both reactions. Thus we get a series of isotherms for heat content as in the earlier problems, although even when no

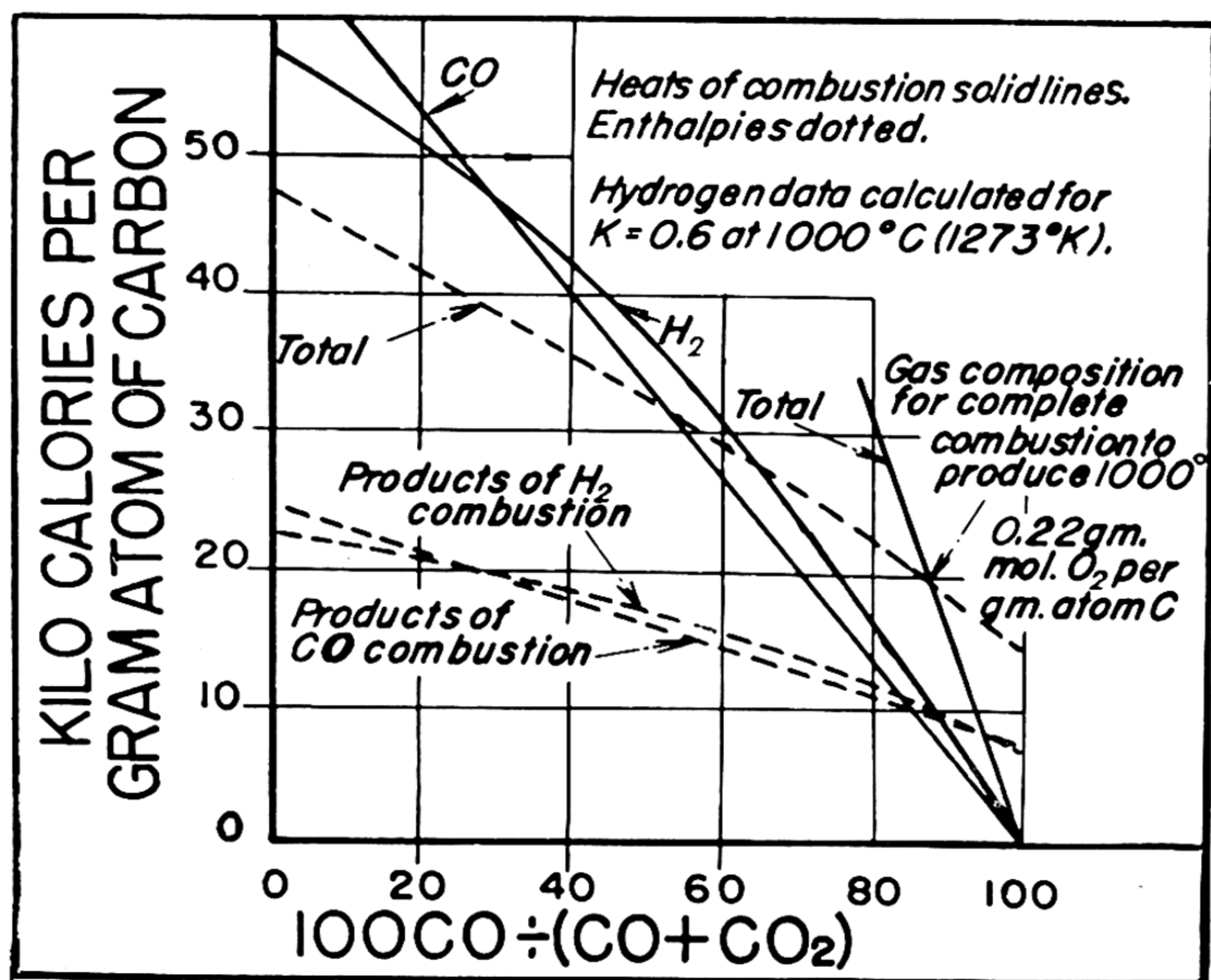


FIG. 11-4. Combustion Conditions of Water Gas with Air near 1000°C.

excess air is needed, the lines will not be quite straight. The heat evolved by combustion cannot, however, be represented by a single straight line as before. This is due to the fact that the CO₂-CO ratio is not identical with the H₂O-H₂ ratio, nor is it necessarily a constant multiple thereof.

The heat evolved by burning CO to CO₂ with various degrees of completion is indeed represented as before by a

straight line, in the present problem joining zero at $\text{CO} = 1$, with the heat of combustion of a gram molecule of CO to CO_2 at $\text{CO} = 0$, as in Figures 11-4 and 11-5.

Similarly, there is a straight line joining $\text{H}_2 = 1$ at zero with the heat of combustion of a gram molecule of H_2O to

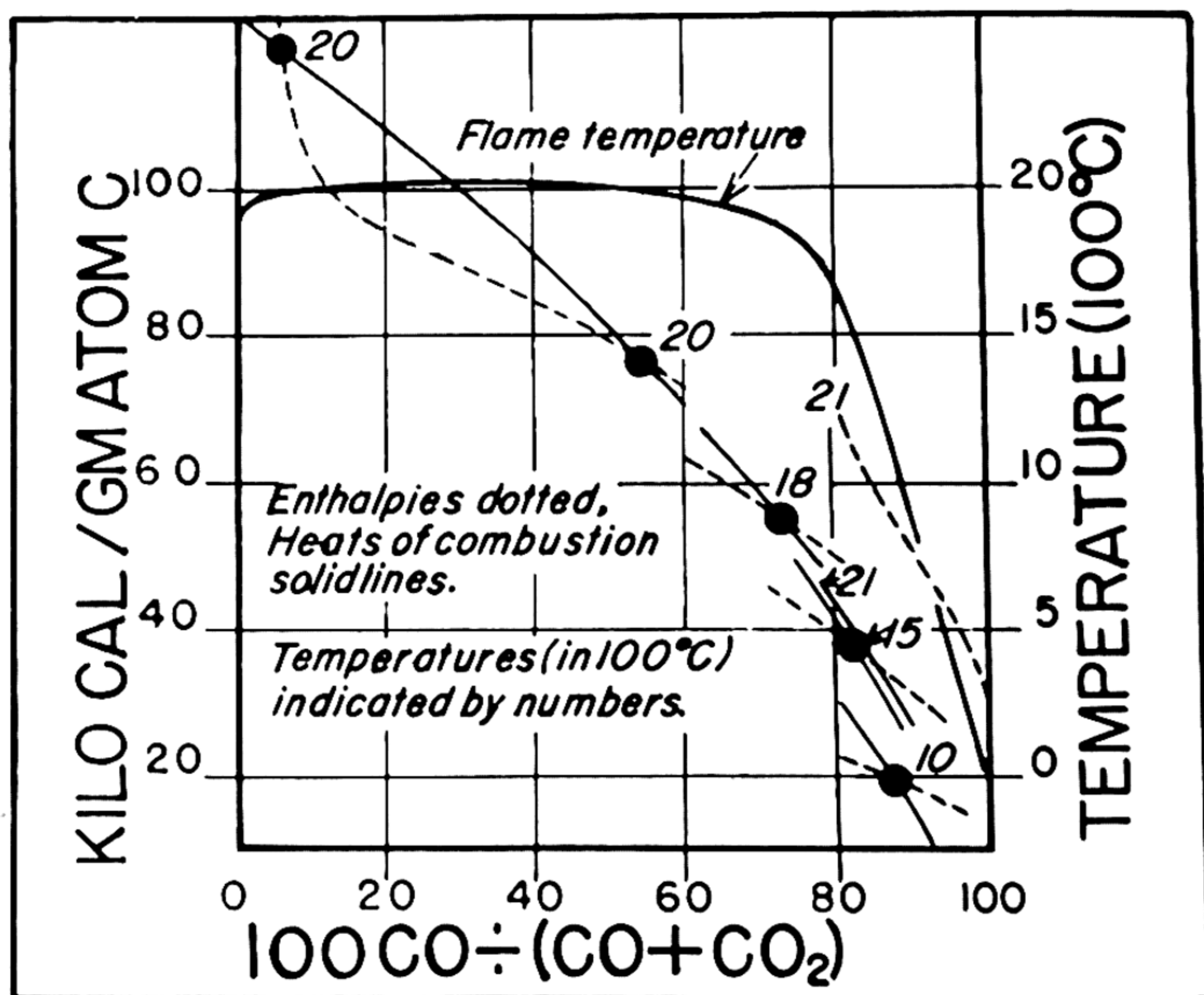


FIG. 11-5. Calorific Effect of Water Gas Burned with Air.

H_2 at $\text{H}_2 = 0$. The two ordinates at a given abscissa are not directly additive, for, as we have said often already, $v_{\text{CO}_2}/v_{\text{CO}}$ is not equal to $v_{\text{H}_2\text{O}}/v_{\text{H}_2}$.

The ordinate at a given CO (or CO_2) concentration must be added to the ordinate at the H_2 (or H_2O) concentration derived from Equation (18), and unless K is independent of temperature, the sum will be different with changing temperature for a constant CO_2 - CO ratio. The difference arises out of the heat of reaction of Equation (16), which

has proceeded to a greater or less extent as the temperature changed.

Thus, instead of having a single line for heat of combustion, we have a family of lines, and to obtain the theoretical temperature of combustion, or calorific effect of water gas, we must find which heat-content isotherm is tangent to the heat of combustion curve for the same temperature.

The combustion of hydrocarbons can be studied in a precisely similar manner, except that in plotting the heat of combustion curve from the relative amounts of C and H_2 present, the heat of formation of the particular hydrocarbon must be deducted from all values.

CHAPTER 12

Relation of Free Energy and the Equilibrium Constant—Activity

SOME APPLICATION of the equilibrium constant K to practical problems having now been made, the reader's understanding of the physical chemistry involved may be helped by some attention to the relation of K to free energy and to its variation with temperature and pressure.

The existence of an equilibrium constant was justified in an earlier chapter on probability grounds, that is, on the chance that certain atoms would react with one another because of meeting by accident in favorable locations. From the principle that systems tend to change spontaneously in the direction that decreases their free energy, we may reason that, if there is a composition, corresponding to the constant K , which is in equilibrium (in other words, incapable of further spontaneous change), it must be in the state of lowest free energy.

Here the student will readily become confused and say, "If a reaction is accompanied by a decrease in free energy,

why is not the completion of the reaction the state of lowest free energy?"

Composition of Minimum Free Energy

Consider a reaction in which only gases are involved. As the reaction proceeds, under constant total pressure the concentration of the reactants, and hence their partial pressure, decreases. The free energy of the reactants thus decreases both because fewer reactants are present and because their molal free energy decreases as a result of decreased pressure.

The products of the reaction, however, increase in amount and hence in partial pressure and in molal free energy. There comes a time when the net increase in free energy of the products increases more rapidly than that of the reagents by an amount more than sufficient to balance the free energy decrease resulting from the further progress of the reaction.

As an illustration, consider the dissociation of CO_2 to CO and O_2 at high temperatures. If we remember the relation of free energy to temperature and pressure given in Equations (3) and (4) of Chapter 6 and the definition of entropy in terms of C_p ,

$$dS = C_p d \ln p, \quad (1)$$

it is possible for us to calculate the free energy of each of the three gases if we know C_p in terms of T . It is also necessary to know the value of S and of F for each gas at some one temperature.

Lewis and Randall teach that for CO or O_2 the molar specific heat C_p is given by

$$C_p = 6.5 + 0.001 T, \quad (2)$$

and for CO_2 by

$$C_p = 7.0 + 0.0071 T - 0.00000186 T^2. \quad (3)$$

Kelley gives the entropies of the three gases at 298°K as $\text{CO}_2 = 50$ cal, $\text{CO} = 45.7$ cal, and $\text{O}_2 = 49.2$ cal.

The International Critical Tables list the corresponding molar free energies at 298°K as $\text{CO} = 39,294$ cal and $\text{O}_2 = 10,230$ cal.

From these figures and the free energy of formation of CO_2 , the latter's molal free energy is determined as 106,159 cal.

From these data the free energies of the three gases at absolute temperature T and pressure p (in atmospheres) are found to be as follows, if the gases are at temperatures where they obey the simple gas law. For CO_2

$$F = -16.1T \log T - 1.132T - 0.00355T^2 + 0.00000031T^3 - 93,644 + 4.554T \log p. \quad (4)$$

For CO ,

$$F = -14.95T \log T - 1.913T - 0.0005T^2 - 27,567 + 4.554T \log p. \quad (5)$$

For O_2 ,

$$F = -14.95T \log T - 5.813T + 0.0005T^2 + 2540 + 4.554T \log p. \quad (6)$$

Using these figures, the free energy of the system CO_2 - CO - O_2 in various states of dissociation has been calculated at a temperature near 2200°K, and the results plotted in Fig. 12-1, which shows a minimum of free energy near the point at which 0.04 mol of CO_2 has dissociated into 0.04 mol of CO and 0.02 mol of O_2 . The values of $\log P_{\text{CO}_2}^2/P_{\text{CO}}^2P_{\text{O}_2}$ are plotted for comparison. Too much precision must not be expected of the graphic representation.

It can be shown that the change of (molal) free energy with pressure at a constant temperature is equal to the molal volume. We have seen that

$$\left(\frac{\partial F}{\partial p}\right)_T = V. \quad (7)$$

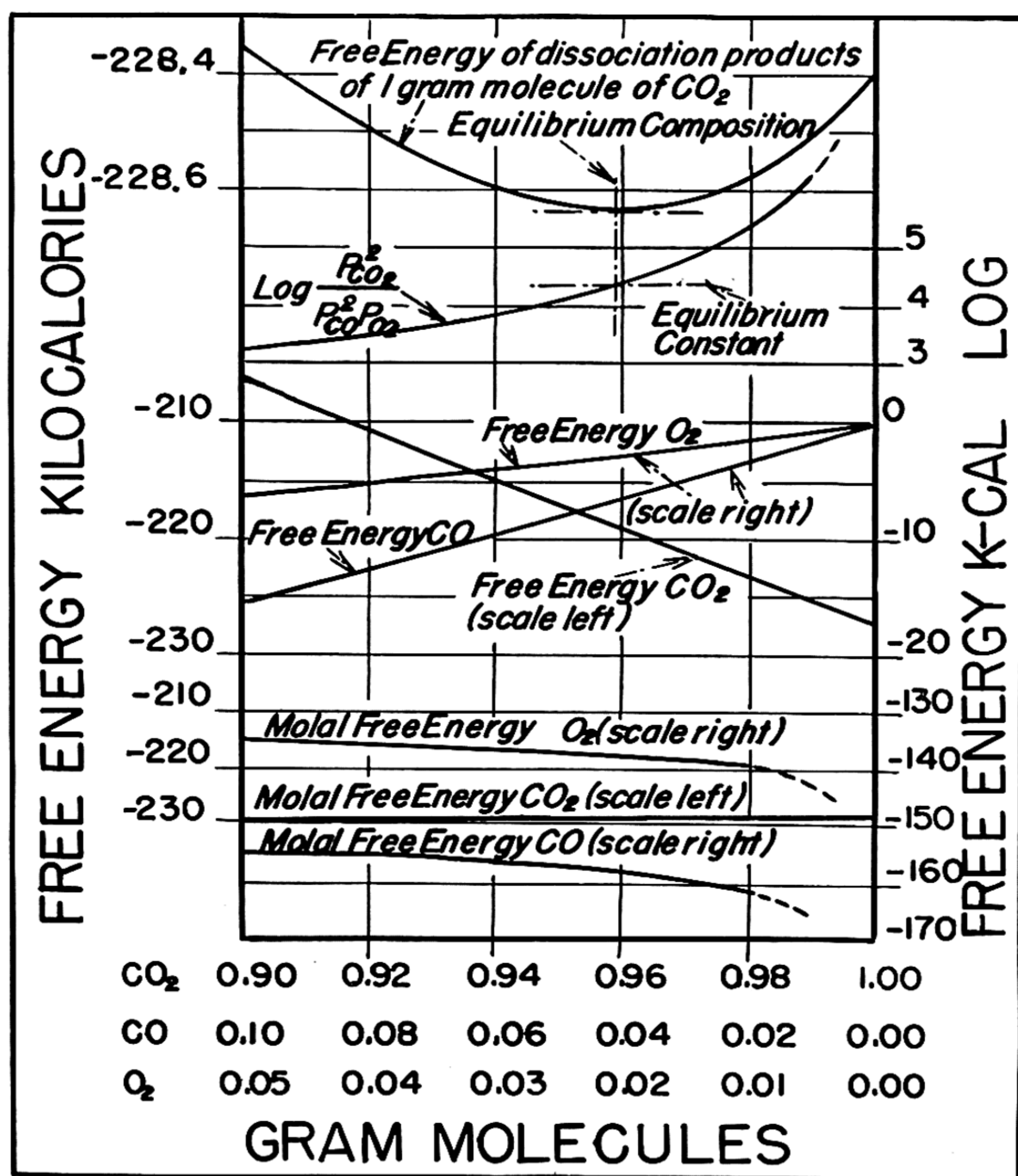


FIG. 12-1. Free Energy and Equilibrium Constant for Dissociation of CO_2 near 2000°C .

Assuming that the gases are ideal gases, which is probably true at such temperatures as we are considering, then

$$V = \frac{RT}{p}. \quad (8)$$

The change in free energy as the pressure changes from p_1 to p_2 is therefore

$$\Delta F = RT \ln \frac{p_2}{p_1}. \quad (9)$$

As usual, R is the familiar gas constant, about 2 cal, and T the Kelvin temperature.

Free Energy and Equilibrium Constant of a Reaction

It can be formally shown that the minimum free energy corresponds to the degree of completeness of the reaction represented by K . It can also be shown that the free energy of the reaction can be calculated from

$$\Delta F^\circ = -RT \ln K. \quad (10)$$

That is to say that the free energy in a system for a reaction proceeding in that direction corresponding to the products appearing in the numerator and the reactants in the denominator in the expression for K has the value shown in Equation (10). A negative ΔF° corresponds to a spontaneous change.

The symbol F° requires comment. It represents the free energy change if the substances are in the *standard state*. The question of a standard state is often open to arbitrary choice. It is the state in which the activity of the substance is taken as unity. For gases, the assumption is usually a pure gas at room temperature and pressure.

Sometimes it is more convenient to choose another constant temperature—for example that at which K has been determined, that is, the temperature corresponding to the T of Equation (10).

The constant K changes with temperature. So far we

have considered it an arbitrary experimental constant. We now see that it is related quantitatively to the free energy, and since the free energy of substances is related to temperature by the equation

$$\left(\frac{\partial F}{\partial T}\right)_p = -S, \quad (11)$$

which says that at constant pressure the free energy changes with temperature at a rate equal to the negative of entropy (at that temperature and pressure), there must thus be a quantitative relation between K and temperature.

It can be shown that

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}, \quad (12)$$

where ΔH is the change in the heat content of the system when the reaction occurs or is the negative of the heat evolved by the reaction.

This equation is equivalent, mathematically, to saying that if $\ln K$ is plotted against $1/T$, the slope is always ΔH . If the Briggs logarithm is used, the slope is $\Delta H/2.3$.

Over short temperature ranges, or if ΔH is constant, such a plot would be a straight line.

If the change in heat content, often called enthalpy, of the reactants for a given temperature change is not equal to that of the products, the heat of reaction will change with temperature.

In many cases the specific heats of the several substances can be expressed by equations as functions of T . Then ΔH can be written as an expression containing T , and Equation (12) can perhaps be integrated. This is usually possible for gases. We have already considered the specific heats of substances.

Pressure and Equilibrium Constant

So far, we have considered the value of K in a gas reaction only at constant (atmospheric) pressure. The relation of

the partial pressures from which K is computed is general, but the corresponding volume relations depend upon total pressure. For example, for the reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, we have

$$\frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 P_{\text{O}_2}} = K, \quad (13)$$

which is an entirely general statement true at all total pressures. The reaction by which 3 mol of gas are converted into 2 mol is accompanied by a decrease of one-third in volume, if the total pressure is kept constant.

If the reaction is at a total pressure of 1 atmosphere, Equation (13) is equivalent to

$$\frac{v_{\text{H}_2\text{O}}^2}{v_{\text{H}_2}^2 v_{\text{O}_2}} = K.$$

However, if the total pressure is π and the volume fractions are now designated w , the partial pressures are $w\pi$ and

$$\frac{(w^2\pi^2)_{\text{H}_2\text{O}}}{(w^2\pi^2)_{\text{H}_2}(w\pi)_{\text{O}_2}} = K.$$

Dividing numerator and denominator by π^2 and transposing π to the right side of the equation, we have

$$\frac{w_{\text{H}_2\text{O}}^2}{w_{\text{H}_2}^2 w_{\text{O}_2}} = \pi K. \quad (14)$$

From the method of derivation of Equation (14), it is at once obvious that the exponent of π is always the difference in the number of molecules on the left and right sides of the equation for the reaction.

Equilibrium Constant in Solutions

The equilibrium constant also has meaning in solutions. Just as we thought of it as being related to the chance of occurrence of a suitable formation of molecules in a gas, so also may we regard it in solutions. Here, however,

the likelihood that a given atom or molecule will be suitably placed is proportional to the number present in a unit volume, which is measured by concentration instead of, as in a gas, by partial pressure.

The concentration is, however, the mol fraction, and when compound formation or polymerization is possibly involved, we must know the molecular formulas or molecular weights of the constituents of the solution, not merely the weight or volume concentration. In dilute solutions this makes no difference, for the molar concentrations will be closely allied to weight or volume concentrations. For higher concentration it will be necessary to consider the proper molecular formula in expressing the concentration.

This similarity of the mass law in its application to solutions and to gases can be expressed in a variety of forms. A common one is that molecules dissolved in a neutral solvent behave as if they alone were present in the total volume. Another old and tried statement is Henry's law, which says that the vapor pressure of a solute is proportional to its concentration. An equivalent phraseology is also known as Raoult's law.

If this is a proper generalization (and with some restrictions if it is not), then since the solution is in equilibrium with its vapor, when equilibrium exists in the latter it exists also in the former, and hence there must be an equilibrium constant for a solution related to that for gases; further, there must be a statement regarding free energy analogous to Equation (10) for gases.

A solution that obeys Henry's law is often said to be *ideal*. In some cases the term ideal implies also that the vapor behaves as an ideal gas in regard to its temperature-pressure-volume relationships.

Often one may wish to solve problems relating to solutions whose vapor does not obey the gas law. These problems could be dealt with effectively in terms of vapor pressure if the vapor were an ideal gas. As an instance,

the free energy accompanying a change of state of a substance, from solid to liquid, for example, is

$$\Delta F_{1-2} = RT \ln \frac{p_1}{p_2}. \quad (15)$$

This is read: "The changes of free energy of a substance accompanying (isothermal) transformation from state 1 to state 2 is the product of the gas constant, the absolute temperature, and the natural logarithm of the ratio of the vapor pressure in state 1 to that in state 2."

The derivation implied that the vapor obeyed the gas law. If it does not we can substitute for the pressure of a gas (here it happens to be the vapor pressure), its *fugacity*. The reader can think of fugacity or escaping tendency as being an artificial concept whose value, when substituted for pressure, corrects for the departure of the gas from perfection.

Except at very high pressures, fugacity f can be calculated from pressure p from the relation

$$f = \frac{p^2}{p_i}. \quad (16)$$

Here p is the existing pressure and p_i is the pressure at which the gas would have its observed molal volume (of course at the same temperature) if it were an ideal gas. That is to say,

$$p_i = \frac{RT}{V}, \quad (17)$$

where T is the observed temperature, V the observed molal volume, and R the gas constant. In perfect gases, obviously—and it may also be seen from Equations (16) and (17)— $f = p$, that is, the fugacity equals the pressure.

If the molecules of solute and solvent (terms that are after all rather artificial) are very similar, it may be assumed that a given molecule would not be either more or less likely to escape from the solution than from the pure

substance (identical with itself). In such a system obviously the vapor pressure, or more accurately its fugacity, would be, by the laws of chance, proportional to its molar concentration. However, if the molecular species were very different, there would be an increasing tendency for it to be retained or rejected. The storage of acetylene, for welding and cutting purposes, is a practical illustration of the fact that a substance in solution may have a very much lower vapor pressure than that corresponding to the presence of an equal amount of gas concentrated into the same volume. The storage cylinder is filled with a very porous absorbent (80% pores) to which is added 43% of the cylinder volume of acetone. The vacant space in the cylinder is then 37% of its empty volume, excluding the absorbent. If 100 cu ft of acetylene is pumped into an empty cylinder of 1 cu ft capacity, a pressure of 100 atmospheres (1500 psi) will result; but if 100 cu ft of (free) acetylene is pumped into the tank containing acetone and absorbent, the pressure will be only 10 atmospheres, even though the acetone expands as it dissolves acetylene. That is, the vapor pressure of acetylene from a solution whose concentration is that obtained by dissolving 100 volumes of C_2H_2 —measured at standard condition in 0.43 volume (measured before solution) of CH_3COCH_3 —is 10 atmospheres. Evidently the acetylene is much more concentrated in the solution than in the gas in equilibrium therewith. At atmospheric pressure acetone dissolves 24 times its own volume of acetylene, and at 12 atmospheres 300 times its own volume. Note that $24/1 = 24$ and $300/12 = 25$, that is, the vapor pressure is nearly proportional to the concentration.

Activity

Gilbert Lewis introduced the concept of *activity* as a substitute for concentration. For ideal solutions activity and concentration are synonymous, but for nonideal

solutions the fugacity is proportional to the activity, and there is an activity coefficient which is the ratio of activity to concentration or a multiple of the relation of fugacity of the vapor to the concentration of a solute. Activity is not an absolute constant, but it is always a relation of activity to activity in some state taken as a standard. In a saturated solution the activity of the solute is that of the pure solute and is unity if the pure solute is taken as the standard state.

The constancy of the equilibrium constants of the mass law depends upon the existence of the ideal state in solution, but similar expressions in which activities are substituted for concentrations are of universal application.

CHAPTER 13

Heat Transfer in Unsteady State

ONE DOES NOT BURN FUEL, except as fireworks, for the mere pleasure of doing so. For practical purposes the heat so generated must be transmitted to some body that we wish to heat. In foundry practice, this may be done to melt the body to make a casting or to heat it for the purpose of heat treating. In other fields, we may wish to convert water into steam for generating electricity, or we may wish to warm air for domestic heating, or we may wish to transfer heat for any of a multitude of other needs.

The principles of such heat transfer are all the same and are much more easily described than applied to actual cases. Two steps are involved in every case: (1) the transmission of heat from the products of combustion or other source to the boundary between these gases and the object to be heated and (2) the transfer into the heated body of heat reaching its surface.

The last-mentioned step involves heat conduction in the unsteady state, which is a more complicated problem than the steady state discussed in Chapter 9 in connection with furnace walls. Long ago Fourier stated the basic principle

that the heat flowing through a body is proportional to the temperature gradient. If we heat one surface of a body above its initial temperature, heat flows in but does not flow out at the opposite surface because some or all of it remains behind, used up to raise the body's temperature within.

Diffusivity

The ability of a substance to absorb heat under such circumstances is measured by a constant called its *diffusivity*, which is a property of the material. This constant, often represented by the symbol h^2 because its square root appears in many formulas, is defined as

$$h^2 = \frac{\kappa}{\rho c}. \quad (1)$$

Here κ is the thermal conductivity of the substance (not to be confused with k , the Boltzmann constant), that is, the number of heat units (calories) that will be transmitted by unit area (1 sq cm) if the temperature gradient is unity ($1^\circ\text{K}/\text{cm}$). The Greek rho, ρ , is the density of the material (grams per cubic centimeter), and C is its specific heat (calories to raise 1 gram 1°K). The fact that all three of these primary constants change with temperature is often neglected for simplicity, but the fact should not be forgotten and, when necessary, values appropriate to a given problem should be selected.

One may say at this point that the determination of the conductivity of a liquid is extremely difficult because of the presence of eddy currents produced by temperature differences. Some help may be found by measuring changes of electrical resistance with temperature by the use of the Wiedemann-Franz equation, which states that

$$\frac{\kappa}{\sigma} = 0.585T \times 10^{-8}. \quad (2)$$

This is to say that the ratio of thermal conductivity κ to electrical conductivity σ is proportional to the Kelvin temperature. The rule appears to be of general application to metallic conductors, in which current is conducted by the motion of free electrons. The units of κ and σ are the reciprocal ohm and the calorie per degree at unit gradient mentioned in Chapter 3.

If we know the diffusivity of a substance, it is more or less simple to calculate its temperature at various times and positions within the body and under various heating conditions. Books have been written on the subject.

Unfortunately the subject cannot be discussed without the use of more complicated mathematics than the reader may like. Fourier developed certain special techniques, called Fourier's series, for dealing with the problem, and some recourse to the calculus is also unavoidable. Furthermore, there is a different solution, often a different approach, depending on the shape of the object and the conditions of heat input. Simple formulas applying to general conditions are, therefore, impossible.

Heating of a Slab

As an example, consider a flat slab of thickness l and of indefinitely great extent in length and width, one of whose surfaces is suddenly heated by Θ° ; required, the temperature at distance x below the surface at time t after the sudden heating. The problem corresponds roughly to a slab of metal lying on a nonconducting hearth, although the instantaneous heating is not realizable. It also corresponds to the same degree (by symmetry considerations) to a slab of thickness $2l$ heated from both sides.

Heat flows in at right angles to the surface. By mathematics beyond the scope of this book, it has been shown that if Θ is the increase of temperature at distance x below the surface at time t after heating the surface by Θ_0 , then

$$\Theta = \Theta_0 \left\{ 1 - \frac{1}{l} \sum_{m=1}^{m=\infty} e^{-h^2 m^2 \pi^2 t / 4l^2} \times \sin \frac{m\pi x}{2l} \cdot \int_0^{2l} \sin \frac{m\pi \lambda}{2l} d\lambda \right\}. \quad (3)$$

This formidable expression gives Θ in terms of an infinite series of terms having the form following the sign of summation Σ (sigma); in this series m has successively all whole number values from zero to infinity. Fortunately, the series converges and generally the number of terms required to reach practically its final value is not prohibitive.

Differentiating to obtain $d\Theta/dx$ to express the temperature gradient at any point x at time t , setting $x = 0$ to obtain the conditions at the surface, and multiplying by κ to get the heat flow per unit area, we wind up with the expression for the rate of heat input per unit time, dH/dt , which may be multiplied by any area desired if the total heat flow is desired. The result is

$$\begin{aligned} \frac{dH}{dt} &= -\frac{\kappa d\Theta}{dx} = -\kappa\Theta_0 \frac{1}{l} \sum_{m=1}^{m=\infty} e^{-h^2 m^2 \pi^2 t / 4l^2} (\cos m\pi - 1) \\ &= \frac{2\kappa\Theta_0}{l} \{ e^{-h^2 \pi^2 t / 4l^2} + e^{-9h^2 \pi^2 t / 4l^2} + e^{-25h^2 \pi^2 t / 4l^2} \dots \} \end{aligned} \quad (4)$$

The heat absorbed in time t by unit area is found by integrating Equation (4) and is

$$H = \frac{2\kappa\Theta_0}{l} \sum_{m=1}^{m=\infty} \frac{4l^2}{h^2 m^2 \pi^2} (1 - e^{-h^2 m^2 \pi^2 t / 4l^2}), \quad (5)$$

where h^2 is the diffusivity of the slab, t the time, and m each odd whole number in succession.

If we wish the temperature at the insulated face only, the expression for Θ becomes

$$\begin{aligned} \Theta &= \Theta_0 \left(1 - \frac{4}{\pi} e^{-h^2 \pi^2 t / 4l^2} \right. \\ &\quad \left. + \frac{4}{3\pi} e^{-9h^2 \pi^2 t / 4l^2} - \frac{4}{5\pi} e^{-25h^2 \pi^2 t / 4l^2} \dots \right). \end{aligned} \quad (6)$$

A little study of this equation and the preceding one will show how successive terms are built up.

One thing to note at once is that the ratio Θ/Θ_0 is determined by the conditions, so that temperatures at given points and times and rates of heat input are proportional to Θ_0 , that is, to the amount by which the surface temperature is raised. Note also the fact that h^2 and t always occur as their product, so that the time to attain a given state is inversely proportional to the diffusivity.

Heating of a Sphere

Other formulas similar to Equation (4) are available for long round rods and for spheres. For spheres the formula is

$$\Theta = \Theta_0 \left(1 - \frac{2R}{\pi r} \left\{ \sin \frac{\pi r}{R} e^{-\pi^2 h^2 t / R^2} - \frac{1}{2} \sin \frac{2\pi r}{R} e^{-4\pi^2 h^2 t / R^2} + \dots \right\} \right). \quad (7)$$

Here r is the radius at which Θ is desired and R is the radius of the sphere.

Schmidt Solution

In order to spare those unfamiliar with mathematics, Schmidt devised a purely graphical method (discussed by Hawkins and Agnew, Research Bulletin 98, Engineering Experiment Station, Purdue University) based on the demonstrable fact that, for flow of heat in one direction only, as in a slab, the temperature at any given time is the average of the temperature, at a time Δt sooner, of two points situated Δx on each side of the given point, provided

$$\Delta t = \frac{(\Delta x)^2}{2h^2}. \quad (8)$$

If, then, one divides, as in Fig. 13-1, the thickness of the slab into an integral number of layers each Δx thick (Δx

may have any convenient value), the original temperature distribution (above the original temperature of the slab) is, as indicated, Θ_0 at the surface and zero everywhere else.

If now we connect the point $x = 0, \Theta = \Theta_0$ with that at $x = 2\Delta x, \Theta = 0$, the intersection of that line with $x = \Delta x$

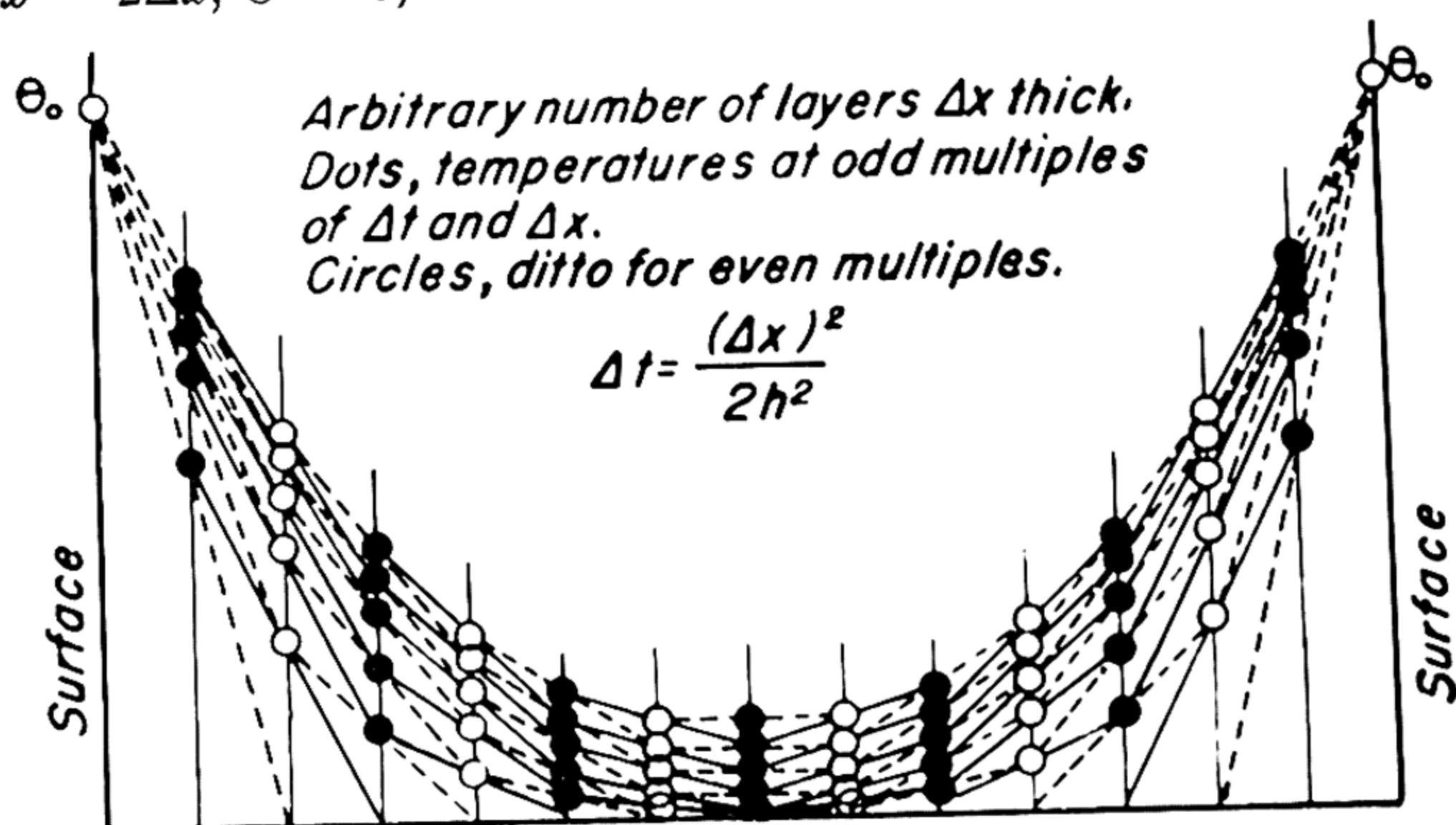


FIG. 13-1. Schmidt Solution of Temperature Distribution at Various Times in a Slab Heated to Constant Surface Temperature from Both Sides.

gives the temperature at Δx below the surface Δt later, when the time interval Δt is computed from the chosen Δx by Equation (8).

If we connect the point so found with $x = 3\Delta x, \Theta = 0$, the intersection of that line with $x = 2\Delta x$ gives the temperature $2\Delta x$ below the surface $2\Delta t$ after starting. If the surface has not changed in temperature, connecting this point with $x = 0, \Theta = \Theta_0$ and also with $x = 4\Delta x$ gives by intersection with Δx and $3\Delta x$ the temperature at these depths after another time interval of Δt has passed.

The process is applicable to the radial heat flow in cylinders if distances from the center are drawn to a logarithmic scale, and to spheres on a reciprocal scale. Certain difficulties arise in these two latter cases with

regard to temperature near the center. The solution is useful, however, especially for hollow objects.

If the heat input into a body is just equal in rate to its diffusion away from the surface, the latter will not change its temperature. Usually it is neither necessary nor possible to maintain this equality. The Schmidt method lets us take care of changes in surface temperature, if known. Instead of having the lines for each temperature interval pass through a single point at $x = 0$, $\Theta = \Theta_0$, each line is drawn to a point in $x = 0$ corresponding to the temperature that existed at that time. Fig. 13-2 illustrates the matter for a uniform increment of temperature $\Delta\Theta$ during each time interval Δt . These solutions are relatively simple if we know the surface temperature in its relation to time.

The slab we studied was considered as a solid. It might as well be a bath of liquid metal. In that case heat transfer through the bath becomes more complicated; not only is there transfer by conduction as just outlined, but also by convection, owing to the bodily transfer of metal by eddy currents in the bath.

A shallow bath heated from above does not naturally set

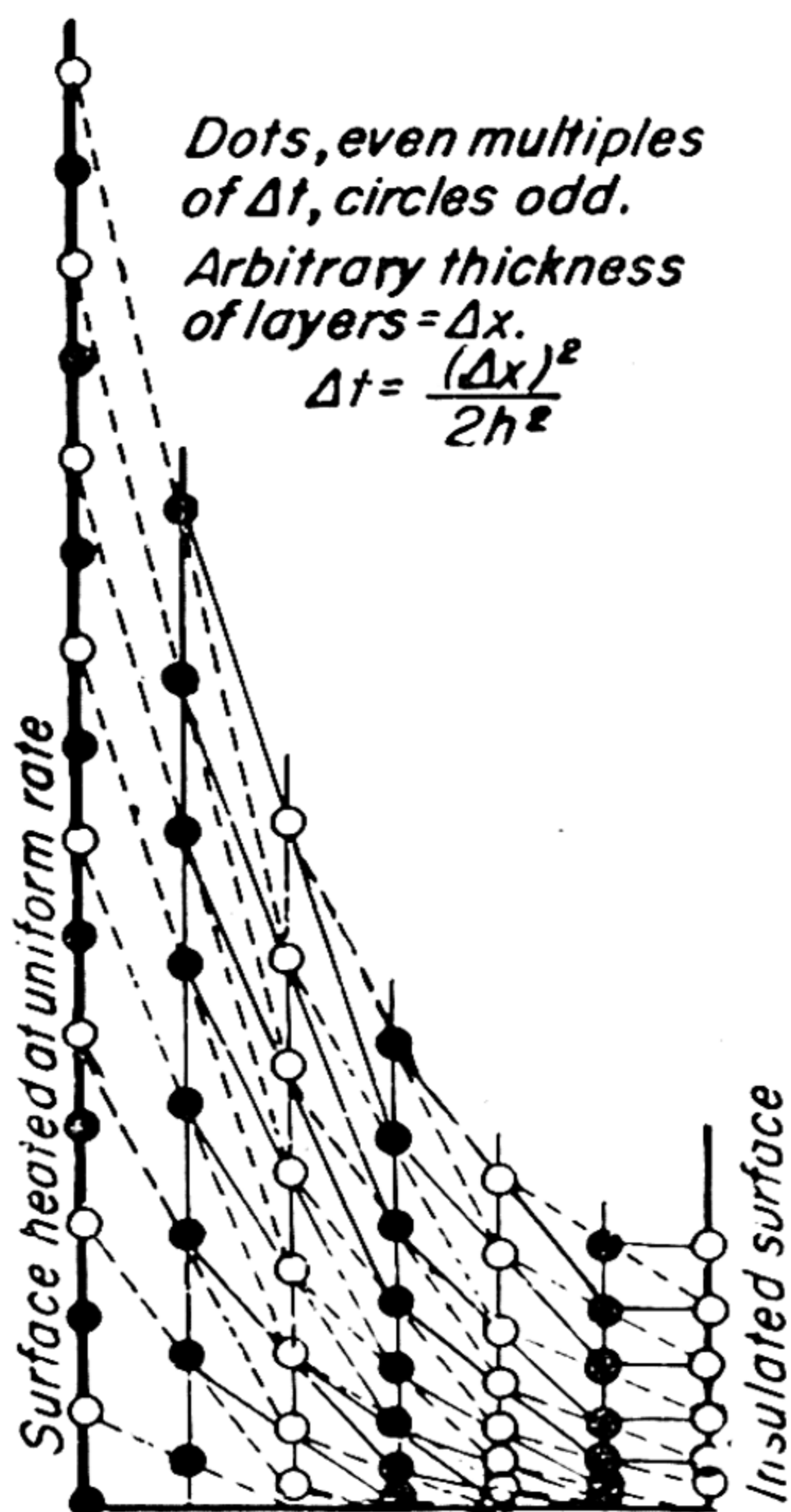


FIG. 13-2. Schmidt Solution of Temperature Distribution at Various Times in a Slab Insulated at the Back, the Front Face Being Heated at a Uniform Rate.

up currents because the hot metal is lightest and is already on top. In reverberatory furnaces the travel of hot gases in contact with the metal tends to drive the upper layers in the direction of flame travel, and hence a current in the opposite direction is formed on the bottom of the bath. Such action, though not suited to quantitative study by calculation, is of importance in the shop.

The changes of surface temperature in a given environment that a given body will undergo are not capable of strict analysis, and the best we shall be able to do is to give some consideration to the principles of heat transfer from the surroundings to an object.

The reader might expect to find here a discussion of the flow of hot gases in furnaces. This would require a digression into the laws of fluid mechanics, which have their greatest application in the pouring of molds. It has seemed best not to disrupt our consideration of heat and its transfer. This matter of heat flow in furnaces is, therefore, left for Chapter 25, when the subject of hydraulics will have been developed.

CHAPTER 14

Heating of Furnace Charges

ALTHOUGH WE SHALL FIND little in the way of practical application, it still is worth while to look into the transfer of heat into a body within a hot furnace.

Such a body absorbs heat by contact with the furnace gases (or liquids if metal or salt baths are involved) and if the furnace contains a transparent atmosphere, by radiation from the furnace walls. Generally the object being heated has a surface temperature below that of the surroundings because heat is being conducted into the body more rapidly than it can be supplied to the surface. Also in many cases the furnace atmosphere is at a lower temperature at the surface of the charge being heated, owing to the abstraction of heat by the latter. This effect becomes less noticeable the more turbulent the flow of gas through the furnace can be made.

Heat Transfer to Charge

It is often not too bad an assumption that the heat input per unit area of the surface being heated is proportional to the difference of temperature of the ambient gas and the

solid metal. The constant of proportionality is called the *coefficient* of heat transfer, here designated by m .

Schmidt's method, introduced in the last chapter, can help us determine the temperature gradients in time and distance.

We select values of Δx and dt by the same principles there described but proceed somewhat differently to draw the figure. In dividing our slab into layers we begin, as in Fig. 14-1, with one whose thickness is $\frac{1}{2}\Delta x$. We also plot an imaginary slab of this same thickness on the outside surface of the slab and place a construction point P at temperature

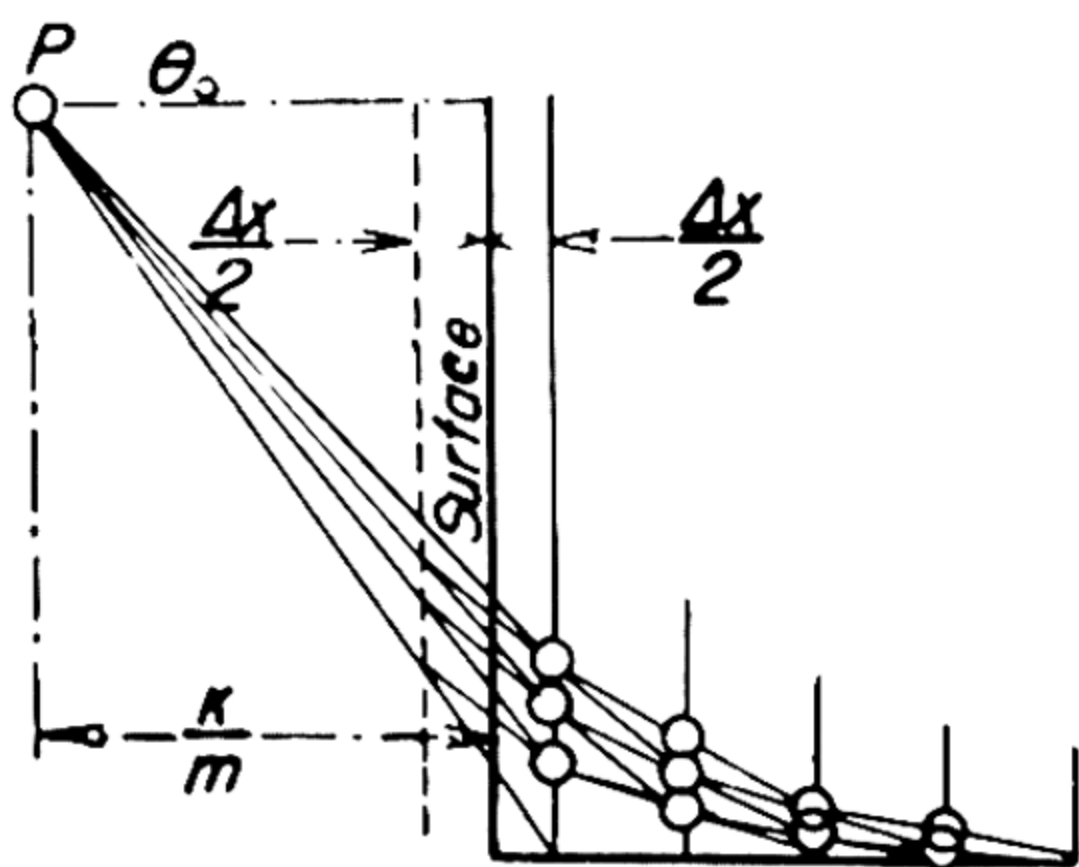


FIG. 14-1. Schmidt Solution of a Slab Heated at a Constant Coefficient of Heat Transfer to the Surface.

Θ_0 (the temperature of the furnace above that of the initial temperature of the slab) and at distance κ/m from the surface. Remember that κ is the thermal conductivity of the body being heated and m is the surface coefficient of heat transfer. At time Δt the approximate temperature distribution is given by joining P with $\Theta = 0, x = \frac{1}{2}\Delta x$. There-

after the construction proceeds as shown in the figure. The problem can even be modified to take care of changing values of Θ_0 (furnace temperature), or of the coefficient of transfer with temperature by plotting successive locations of P , as will be obvious by a study of the figure.

Actually, the basis of Fig. 14-1 is oversimplified. The rate of heat transfer increases with the velocity with which the gas flows over the surface and depends largely on the roughness of the surface. We evaded all these difficulties by assuming that we know m for any given problem, when we really do not.

Heat Transfer by Radiation

When high temperatures are involved, the transfer of heat (from an incandescent flame or from the furnace roof) by radiation is the major consideration. At any temperature (except the absolute zero), bodies give off radiant energy. The amount of energy radiated per unit surface in unit time is proportional to the fourth power of the temperature (Stefan-Boltzmann equation). It depends also upon a property of the body called *emissivity*, which is the ratio of the energy emitted to that which would have been emitted by a black body at the same temperature. This emissivity is always less, and often much less, than one.

When radiation falls on a body, some is absorbed and some is reradiated.

The ratio of the emissivity and the absorption coefficient is a constant for all substances, depending only on the wavelength of the radiation and the temperature. This being so, this ratio must be the emissivity of a black body under the existing conditions, since a body is black if it absorbs all the rays falling upon it, that is, if it has an absorption coefficient of one. Readers in this field are reminded that the foregoing principle is called Kirchhoff's law.

The coefficient σ in the Stefan-Boltzmann equation,

$$S = \sigma T^4, \quad (1)$$

where S is the total radiation emitted (not entropy as elsewhere previously) and T is the absolute temperature, is numerically equal to

$$1.378 \times 10^{-12} \text{ cal/cm}^2/\text{sec}/^\circ\text{K}^4,$$

which represents the amount of energy radiated by a black body in terms of its area, temperature, and time. This value can be derived from fundamental constants.

This figure assumes that radiation is *in vacuo* or in air (whose index of refraction is practically 1). Radiation in a medium of some other refractive index, n , is proportional to n^2 .

The foregoing principles can be applied to the heat transferred to a given area at a given temperature if it received radiation from surroundings at a given higher temperature. The relation is expressed by

$$H = kt[T_1^4 - T_2^4]. \quad (2)$$

Here H is the heat radiated in time t to the unit area of a surface at temperature T_2 from surroundings at T_1 , and k represents the coefficient of absorption of the surface. It is implicit in this equation that the area of the surrounding walls is at least as great as that of the object being heated, which is always true for a commercial furnace containing a single piece or densely packed small pieces. If some of the charge is protected from direct radiation by other parts, the areas so shaded do not participate in heat transfer.

As the temperature within the furnace becomes more and more nearly uniform, the constant k approaches black-body conditions.

Trying to make any calculations about the flow of heat from a moving stream of gas to its surroundings is usually not labor well spent. Especially if the stream is drawn, as in a chimney, by differences of density of the gas due to temperature differences, the calculations become very involved and recourse must be made to constants that actually are guesses. The fact that the calculations are never of general application proves that they concealed errors due to variables with which one has not worked properly.

Preferred Direction of Flow in Passages

This, however, is a good place to consider a qualitative principle, further discussed in Chapter 25, that is all too frequently ignored in planning for uniform heating of a charge. Suppose we wish to heat, uniformly and efficiently, a body of material containing various vertical passages through which hot gas may pass. If by chance one of these

passages is hotter than another, the ambient gas will flow upward in the hotter one and downward in the colder one. Now if heat is supplied above the charge and the flue takes gas off at the bottom, then the downward stream in the cold passage will bring in heat, and the upward flow in the hot passage will prevent further inflow of hot gas; thus the two passages will tend toward the same temperature.

If heat is admitted at the bottom, it will seek the already hotter zone and accentuate the difference in temperature.

When radiation from flame to stock is involved, luminous flames should be used. The fact that a flame is luminous indicates that it is radiating energy vigorously.

Clear nonluminous flames heat mainly by conduction, heat being transmitted to stock and furnace structure and radiating from the latter.

Flames are luminous when they carry solid particles, usually carbonaceous, which are heated by contact and act more or less as black-body radiators.

Measurement of High Temperatures

AN IMPORTANT APPLICATION of the principles of radiation is in connection with the measurement of high temperature.

In principle, the absolute or Kelvin temperature scale stems from the kinetic theory of gases and from the relation that for an ideal gas the well-known equation of state implies that

$$T = \frac{pV}{R}. \quad (1)$$

The selection of the particular increment of energy representative of a degree was originally arbitrary and comes out on the absolute Centigrade or Kelvin scale if in Equation (1) pressure is in atmospheres, V is the volume of a gram molecule of an ideal gas, and R , the gas constant, is in calories.

Although no gases are ideal throughout a long range of values of p and T , a number of gases exist for which either the agreement is satisfactory in usable temperature ranges or the deviations from Equation (1) are known and can be applied as corrections.

Thermocouples

The gas thermometer, however, is ill suited to commercial use, and moderately high temperatures are usually measured by thermocouples whose operation will be familiar to all. The electromotive force generated by a couple whose cold junction is at zero absolute and whose hot end is at temperature T , can be arbitrarily represented by an equation such as

$$E = a + bT + cT^2. \quad (2)$$

The numerical values of a , b , and c can be determined from observations of E at three or more values of T known by some derivation, direct or indirect, from gas thermometer temperatures.

The form of Equation (2) is purely empirical and has no theoretical meaning.

The cold junction of a thermocouple is, of course, never at 0°K and rarely at 0°C , so that a correction is necessary to obtain correct values of T from E .

Sometimes this is done by determining a , b , and c with the cold junction at 0°C or at some other value such as 15°C or 20°C and using the couple under corresponding conditions. In principle, it is well to remember that according to Equation (2) the electromotive force of a thermocouple with its hot end at T and its cold end at T_c will be

$$E = b(T - T_c) + c(T^2 - T_c^2). \quad (3)$$

The equation is given to indicate that if, for example, the available equipment is calibrated to read correctly temperatures when the cold junction is at 0°C , it *does not suffice* to add to the readings the cold-end temperature if that differs from zero. Evidently Equation (2) is very sensitive to errors in c at high temperature. It is fortunate, therefore, that the radiation laws give us a high-temperature scale independent of reference to absolute measurements based on the gas thermometer.

Radiation Laws

The simplest of these is an application of the Stefan-Boltzmann law. A hollow box (or furnace), at uniform temperature throughout and having a small window, sends radiation from that window in accordance with black-body laws.

If the radiation given out by a known area is measured, then the Stefan-Boltzmann equation of the last chapter gives the temperature.

A method that is often preferable is based on the principle that the color of light emitted by a hot body, that is, the wave length of the radiation it gives off, varies with temperature. For the old-time blacksmith's cherry red, blood red, orange, white, and blue heats, the physicist now substitutes more definite concepts of the relation of color and temperature.

The distribution of the energy radiated by a hot body over the entire spectrum of wave lengths is well understood and depends upon the temperature. There is one wave length, λ_m , for which the radiation is of maximum intensity.

These wave lengths are related to temperature by the expression (Wien's displacement law),

$$\lambda_m T = 2.88 \text{ (cm}^\circ\text{K)}, \quad (4)$$

in which T is in $^\circ\text{K}$.

It is quite possible by spectroscopic measurements to find the wave length of the most intense radiation, which may be in the infrared or in the visible spectrum, and so deduce the temperature of the radiator.

Be it well remembered, however, that the principle is applicable only to bodies that radiate a continuous spectrum. Glowing gases that emit radiations of characteristic frequencies (line spectra such as are used in chemical analyses) have their characteristic wave lengths determined by energy changes within the atom and do not come within the field of Wien's law.

CHAPTER 16

Vaporization and Oxidation of Alloys

THINGS WOULD BE much pleasanter for the foundry metallurgist if the molten metals would only remain unaltered in composition.

Although the steel foundryman in most cases wishes to produce chemical changes by his processes, his brothers in most other fields would be gloriously happy if they could only mix solid metal in proportions to give the desired composition, melt it, and cast the product.

Nature is not so simple. The principal causes for undesired changes of composition are vaporization and oxidation, although in cupola melting of cast iron, carburization is also to be considered.

In an earlier chapter we learned that all substances have a vapor pressure that is related to the temperature. This vapor pressure is the partial pressure of the substance in the ambient atmosphere when the latter contains just enough molecules of the substance so that, by the operation of

chance, molecules enter and leave the substance at the same rate.

In ideal solutions the vapor pressure of a solute at a given temperature is proportional to its molar concentrations so long as this rule holds, if we know the vapor pressure of a pure substance at a given temperature, then in a solution containing a particular mol fraction of that substance its vapor pressure is the product of the existing mol fraction and the vapor pressure of the substance in the pure state.

Here we become involved in the question of molecular weights and enter on the somewhat disputed field of whether liquid metals contain molecules. These problems would have to be resolved before we could make full use of the principles under discussion.

In Equation (2) of Chapter 5 the equation correlating vapor pressure with temperature was quoted.

In Chapter 12 the concepts of activity, fugacity, and the activity coefficient that can be used for nonideal solutions were described.

Slags are frequently considered to be nonideal solutions of very simple molecular types in one another. Chipman, however, has pointed out important instances where assumptions of more complex molecular species would yield constant activity coefficients for varying molar concentrations.

Similar conditions may exist in metallic solutions. In any event, if activities are substituted for concentrations, the usual equilibrium laws remain valid even for nonideal solutions.

Vaporization in Melting

Returning, after this brief digression, to the vapor pressure (or fugacity) of a component of a solution, we find that it rises with concentration and temperature. If we heat a substance in a closed container, enough of the substance will vaporize to produce the corresponding vapor pressure in the enclosed atmosphere, and evaporation will stop.

If some of the substance is constantly removed, more will continually evaporate, and the solution will be depleted in the more volatile constituent; that is, that of highest vapor pressure.

One is not surprised when such metals as zinc can be distilled but other metals, not usually thought of as volatile, behave similarly. The boiling point of manganese is 1900°C ; that is, its vapor pressure is one atmosphere at that temperature. The manganese content of steel (boiling point of iron 3000°) can be reduced to a few hundredths of one per cent by distillation into a partial vacuum of a few thousandths of an atmosphere.

Only the partial pressure of the element enters into this picture, for the vapor pressure of a substance, though varying with temperature, is nearly independent of total pressure.

The very recent interest in magnesium-bearing cast iron, shown in Fig. 20-12, emphasizes the importance of vapor pressure considerations in foundry operations. Magnesium boils at 1110°C , yet it is desired to retain, a low concentration in iron at 1400°C . This is known to be possible, especially, according to Harold Bogart, if the ladle is far from full. How can this be?

From Trouton's rule, for vaporization, discussed in Chapter 5, the latent heat of vaporization of magnesium should be about 30,426 cal/gm atom at 1383°K (1110°C). From the Clapeyron-Clausius equation (2) in Chapter 5, its vapor pressure at 1673°K (1400°C) is about 6.5 atmospheres.

Assume that 0.07% Mg by weight is to be retained; this is 0.133 atomic per cent since the atomic weight of iron is about 1.9 times that of magnesium. If the solution is atomic and ideal, that is, obeys Henry's law, the vapor pressure of magnesium from the alloy will be $0.00133 \times 6.5 = 0.0086$ atmosphere. The total pressure of gas on the ladle is, of course, one atmosphere, so that it must contain 0.86% by volume of metallic vapor to retain the desired magnesium content.

The vapor is strongly reactive with both N_2 and O_2 and may also be carried off by convection currents, but it seems possible, by minimizing the latter, to maintain a suitable atmosphere for a considerable time. It is also to be considered that the top of a partly filled ladle may be far enough from the metal so that the temperature there is below the boiling point of magnesium which is then returned as droplets to the surface.

Such an alloy should not be able to evolve magnesium vapor below the surface of the liquid when the pressure of necessity exceeds one atmosphere. Bubbles of some sort do, however, frequently form inside the skin of frozen castings, possibly because of the existence of subatmospheric pressure when the liquid metal shrinks inside the frozen shell. Alternatively the bubbles may be some other gas and not magnesium vapor.

Generally the foundryman is concerned with oxidation as a matter of slag reactions. These reactions are discussed in Chapter 17 in connection with steelmaking processes. This is a good place, however, to introduce consideration of how metal is oxidized by furnace atmospheres.

Oxygen Pressure

All the metallic oxides have dissociation pressures. If they are heated, oxygen is given off until for a given temperature the partial pressure of oxygen has some particular value. Conversely, if either solid or liquid metal is exposed to an atmosphere whose partial pressure of oxygen is higher than the dissociation pressure of its (lowest) oxide, that oxide is formed at the surface.

Conceivably, the oxide dissolves in the metal, but then more and more oxide is formed until the metal is saturated and an oxide forms on the surface.

If the temperature is high enough and the pressure low enough, any oxide should be capable of giving off its oxygen and being converted to pure metal. Actually, the tem-

perature and pressures, with few exceptions, are not attainable. Priestley's experiment, in which he heated HgO to a temperature where its dissociation pressure was above the pressure of oxygen in the atmosphere, is a famous exception.

In discussing combustion we found that, in general, at flame temperature we encounter the presence of some O₂ in order that the equilibrium



might be obtained. Such atmospheres will oxidize a metal if the partial pressure of O₂ is greater, as it often is, than the dissociation pressure of the oxide.

The reaction of iron with carbon during melting is best considered two chapters later in connection with the iron-carbon system. First, it will be well to learn more of some important chemical reactions.

Direction of Reactions

METALLURGISTS NEED to know in what direction reactions will go, how fast, and how far. Since in many cases processes are carried on too rapidly to reach completion, the first is the most important.

Direction of Reactions

All processes proceed spontaneously in the direction that reduces the free energy of the system. This has been said before but will bear repeating.

In Chapter 6 we learned that F , the free energy of a substance or of a multiplicity of substances forming an isolated system, is related to the heat content of the system and to its entropy, that is, the unavailability of its heat content, and to enthalpy, H , by the equation

$$F = H - TS. \quad (1)$$

Recall that H and S are calculable from specific-heat data.

Free Energy of a Reaction

Subtracting the value of Equation (1) for a system before a reaction begins from its value after the reaction is com-

plete, we write, for changes in the three constants,

$$\Delta F = \Delta H - T\Delta S. \quad (2)$$

The equation applies to an isothermal process, and if the process is carried out reversibly, it can be applied to the calculation of the free energy of the reaction. If ΔF is negative, the reaction will proceed spontaneously.

When $\Delta F = 0$, the reaction has gone to equilibrium.

Reversible Processes

The concept of a *reversible* reaction can be made the subject of lengthy philosophic speculation. Perhaps it can be approached indefinitely closely but not reached. The reader can visualize its meaning by remembering that it represents carrying on the process under conditions that at no time leave the system more than an unimaginable small degree away from equilibrium.

This means that all but the smallest gradients of temperature, electromotive force, concentration, and other factors with time

and space are to be eliminated. This implies that the process be carried on very slowly.

The reason that such a matter need be considered is that although ΔF and ΔH are dependent only on the beginning and final states of the system, the work done can vary according to the path the system takes in changing from one state to the other, and only the reversible path gives the maximum of available mechanical work, and hence the entropy.

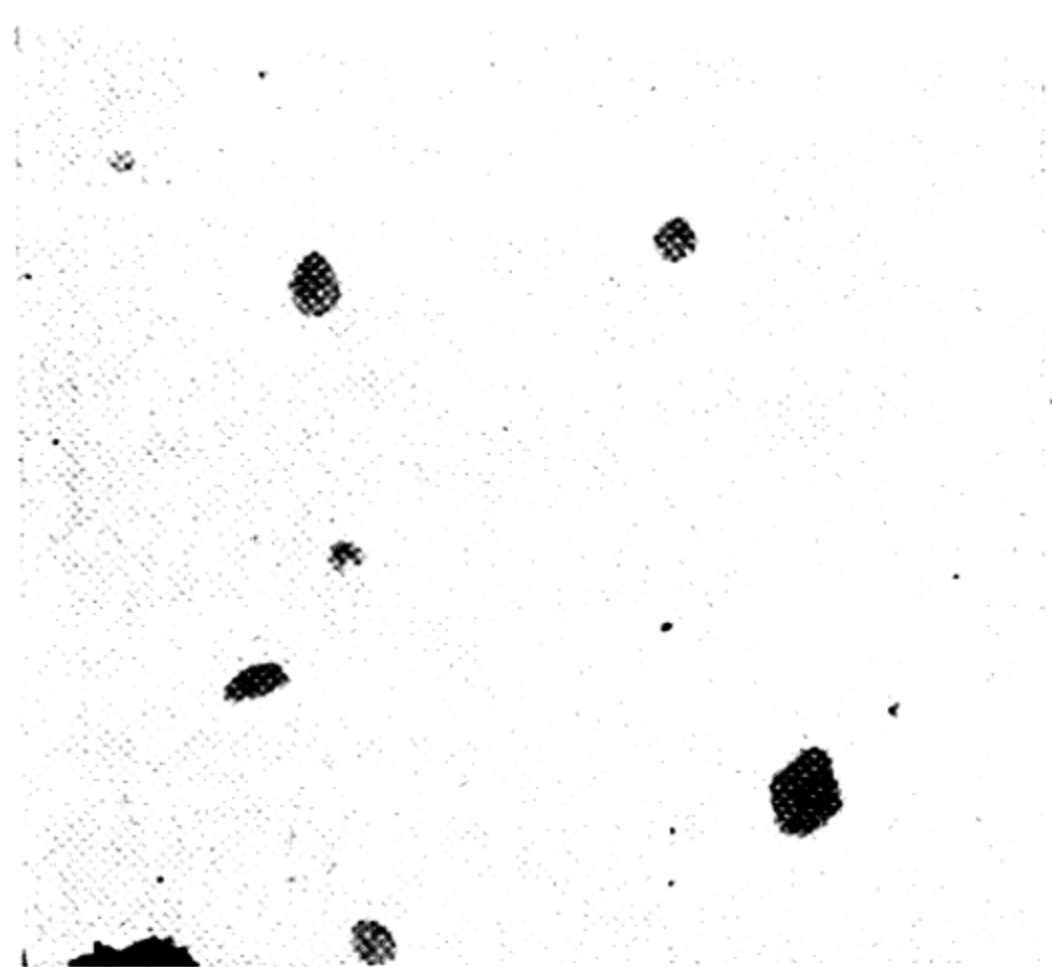


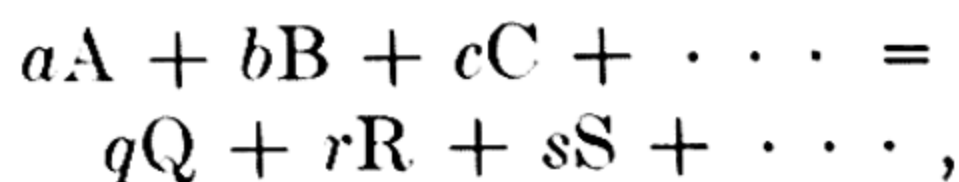
FIG. 17-1. Manganese-Iron-Oxygen-Sulphur Complex in Medium Carbon Steel. 500 \times ; Unetched.

Readers often think that ΔH must be zero for an isothermal process. This is a mistake, for even if the temperature does not change, the mean heat capacity may do so. Melting or boiling are examples.

A discussion of how we know the free energies of reaction would take us somewhat far from the foundry metallurgist's activities.

Equilibrium Constant

In Chapter 10 we became acquainted with the law of mass action as applied to gases. A similar law applies to substances in solution. If we have a reaction in which a molecules of substance A react with b molecules of B and c molecules of C, and so on to produce q molecules of Q, r molecules of R and s molecules of S, and so on, which might be written



then the reaction will attain equilibrium when

$$\frac{[Q]^q[R]^r[S]^s \dots}{[A]^a[B]^b[C]^c \dots} = K, \quad (3)$$

where K is called the equilibrium constant of the equation and is independent of the absolute values of Q, R, S, A, B, and C. In Equation (3) [Q] means the

FIG. 17-2. Grainboundary Inclusions of Manganese-Iron-Sulphur Complex in Medium Carbon Steel. 500 \times ; Unetched.

molar concentration of substance Q in solution or, for a non-ideal solution, the activity of Q in the solution. In the latter case some write a_Q^q instead of $[Q]^q$.

In the earlier chapter, an outline was given showing that such an equation as now written [Equation (3)] would repre-

sent a stage of completion at which ΔF for the reaction became zero. On one side of this relation the reaction would proceed in one direction and on the other, in the opposite direction. Equilibrium is implied.

Having merely indicated that the mass law and free energy have a logical relation, we turn to the former for help in studying these reactions.

Most foundry practices seek to avoid chemical reactions that produce changes of composition. The steel foundry constitutes an exception, for it must deliberately remove carbon from the charge and finally deoxidize the metal. Basic melting also involves removal of phosphorus and/or sulphur. Actually, these

processes involve reactions between slag and metal, but for a beginning we may consider the problem as one of reactions between compounds dissolved in molten iron.

Nernst Partition Principle

This follows from the so-called Nernst partition principle which states that the ratio of (molar) concentration of a given solute in solution in two different solutes (thus forming two solutions that do not mix) will be a constant. More rigidly speaking, "activities" should be substituted for "concentrations."

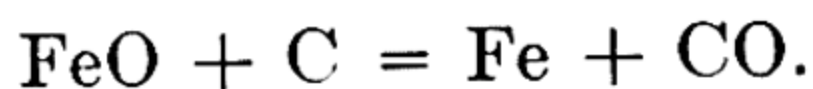
Carbon-Oxygen Equilibrium in Steelmaking

Now at meltdown a steel bath contains carbon from the charge in solution and also has dissolved in it ferrous oxide



FIG. 17-3. Eutectiform Inclusion of Manganese-Iron-Sulphur Complex in Medium Carbon Steel. 500 \times ; Unetched.

(FeO) from the slag. These usually wish to react according to the formula



The mass law then says that equilibrium will be reached when

$$\frac{[\text{Fe}]P_{\text{co}}}{[\text{FeO}][\text{C}]} = K_1. \quad (4)$$

But the CO escapes as bubbles of that gas whose pressure is but little above atmospheric, and the mol fraction of iron is nearly constant and nearly unity; hence one can say (with near accuracy) that

$$[\text{FeO}][\text{C}] = K_2. \quad (5)$$

This constant has actually been determined by a number of observers. Expressed as the product of oxygen and carbon, both in weight per cent instead of in mol fractions as above, this product is probably near 0.005% for low carbons at the temperature of molten steel.




FIG. 17-4. Manganese-Iron-Sulphur Grainboundary Film in Medium Carbon Steel. 500X; Unetched.

This equilibrium constant is found to increase with increasing carbon, which has been explained by the fact that the product of the mol fractions in Equation (5) is not directly proportional to weight fractions, that carbon may be present as either or both C and Fe₃C, and that CO may be soluble in iron.

The constancy of product of the FeO and C concentration in the iron implies that equilibrium is attained in the steel melting process. It has been rather definitely established, by observing the oxygen and carbon contents of a heat during decarburization, that this product may vary widely

and that the oxygen content of the bath is more closely related to its Mn and/or Si contents than to its carbon content. A variety of ingenious explanations have been formulated, all of which consider the mechanism of the removal of CO as bubbles. Our derivation involved the thought that the bath is in equilibrium with CO at room pressure. The formation of a bubble within a liquid involves considerable energy because of surface tension and other forces whereby the effective pressure of CO is increased at the surface between gas and metal. Such a process may well result in failure to attain equilibrium from the high carbon side and may explain the frequent occurrence of carbon and oxygen, with products far too large.

On the other hand, more experimenters than one have found that the rate of carbon removal can be used to measure the oxygen content of metal. Perhaps the circumstances were favorable for the attainment of equilibrium.

Our present purpose does not warrant detailed discussion of the physical chemistry involved. After removing carbon, usually to a fairly low figure, it is often necessary to remove excess oxygen in order to get quiet steel. This may be done by adding any readily oxidizable element, such as Mn, Si, Al, Ti, and so on.

Deoxidation by Manganese

For example, if Mn is added, the reaction $\text{Mn} + \text{FeO} = \text{MnO} + \text{Fe}$ will take place and its equilibrium constant will be



FIG. 17-5. Manganese-Iron-Aluminum-Sulphur Complex in Medium Carbon Cast Steel. 500 \times ; Unetched.

$$\frac{[\text{MnO}]}{[\text{Mn}][\text{FeO}]} = K_3. \quad (6)$$

If equilibrium is reached, the relation $\left[\frac{\text{MnO}}{\text{FeO}}\right]$ in the metal will be proportional to the relation $\left(\frac{\text{MnO}}{\text{FeO}}\right)$ in the slag.

Since both Mn and C may remove oxygen under given conditions, either Equation (5) or Equation (6) may correspond to the lower value of oxygen in iron. It is the intent of the deoxidizing process that Equation (6) shall produce the lower oxygen.

It is instructive to note that if both reactions are to give the same FeO, then from Equation (5)

$$[\text{FeO}] = \frac{K_2}{[\text{C}]},$$

and from Equation (6)

$$[\text{FeO}] = \frac{[\text{MnO}]}{[\text{Mn}]K_3}.$$

The two values of FeO must be equal, that is,

$$\frac{K_2}{[\text{C}]} = \frac{[\text{MnO}]}{[\text{Mn}]K_3},$$

or

$$\frac{[\text{MnO}][\text{C}]}{[\text{Mn}]} = K_2K_3 = K_4. \quad (7)$$

The amount of manganese to be added to steel of a given carbon to prevent the formation of CO is a function of the MnO dissolved in the metal and hence of the slag composition.

The values of the various equilibrium constants change with temperature, and the amount of a given deoxidizer that will reduce the oxygen to some particular value thus depends on temperature. It can readily happen that the relative ability of two elements to deoxidize steel may

change so greatly with temperature as to reverse their rank for this purpose.

Basic and Acid Slags

The amount of FeO in steel depends in part on that in the slag but also on the other chemical characteristics of the slag. Acid slags are, in the main, solutions of (MnO)(SiO₂) and (FeO)(SiO₂) in each other. Neither is soluble in iron to any marked degree. If lime is added to the slag, some of the SiO becomes converted into (CaO)₂SiO₂, the lime substituting for FeO or MnO, which can then dissolve in the mixture of silicates. These free oxides in solution divide between the slag and steel in accordance with the Nernst partition principle, and the oxides dissolved in the steel are active decarburizers.

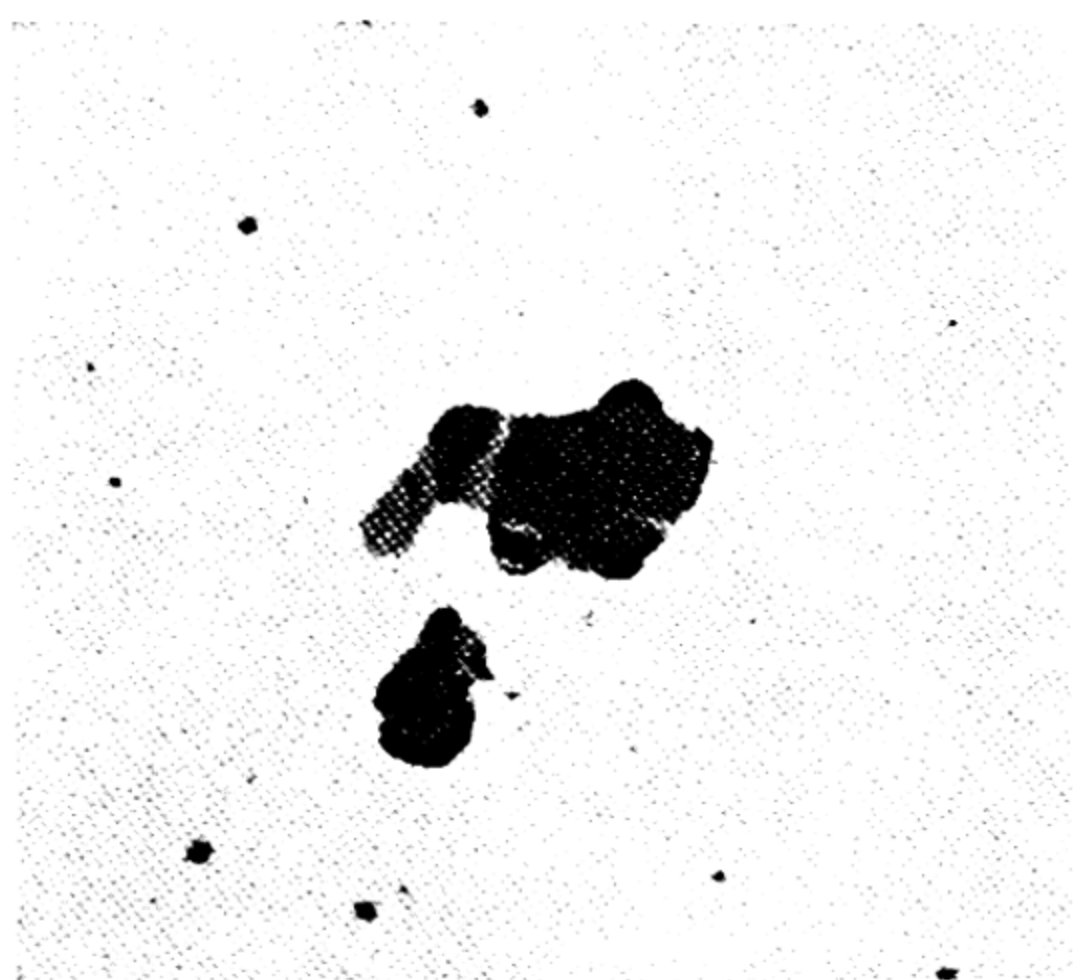
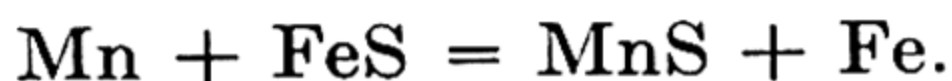


FIG. 17-6. Duplex Sulphide in White Heart Malleable. Largely Iron, Sulphur, and Oxygen. 1000× (Oil Immersion); Unetched.

Manganese Sulphide

Another reaction of great importance to the steel foundryman is



At furnace temperature this reaction goes to the left and the resulting FeS dissolves in steel. The addition of manganese can then not desulphurize the steel. As the temperature falls, the reaction proceeds more and more to the right, and the lesser solubility of sulphur complexes high in manganese and the lower temperature cause these substances to separate out as a separate phase. Some may

rise into the slag, but much is trapped in the freezing metal.

Since oxygen is likely to be present, the substances are actually mixtures of sulphides and oxides of manganese and iron dissolved in one another.

When they are relatively rich in oxygen and manganese, they freeze into droplets before the steel solidifies. When low in manganese, they remain liquid until they have been trapped into grain boundaries during freezing.

Deoxidized steels are thus likely to contain grain boundary sulphides that weaken the metal. When the deoxidizing agent is aluminum and an excess of, say, from 0.02% to 0.05% of that metal remains after deoxidation, it passes into the sulphides and raises the freezing point, thus keeping them from being scattered all over the grain boundaries.

The sulphides containing aluminum are somewhat angular in character, suggesting that perhaps they crystallize out of the metal instead of separating as a liquid.

The removal of phosphorus from liquid steel requires slags high in lime and in iron oxide to convert that element into tricalcium phosphate. If the slag is not kept basic, phosphorus may revert from slag back to metal. The equilibrium constants are so related to temperature that the reaction proceeds best at lower temperatures, which is rather unusual.

Solubility of Gases

The concentration of a dissolved gas is of course proportional to its partial pressure in the ambient atmosphere. The diatomic gases, H_2 and N_2 , dissolve as atoms; hence their solubility is proportional to their concentration and degree of dissociation and hence to the square root of their partial pressure. From the mass law the concentration of atoms is proportional to the square root of the concentration of molecules.

CHAPTER 18

Rate of Reactions

MOST FOUNDRY PROCESSES are conducted too fast for equilibrium to be reached. In such cases the reactions go toward the conditions discussed in the previous chapter but may not come near reaching these completely.

Laws can be worked out for the velocity at which a reaction goes on if the reactants are kept thoroughly available to each other, as in a well-mixed liquid.

Thermal Coefficient of Reaction Velocity

Reaction rates in gases are proportional to $e^{-Q/RT}$, where Q has the dimensions of energy.

The effect of the negative sign, since Q is a positive number, is that the logarithm of the rate varies inversely, as $1/T$.

Experience has shown that this also applies well to many reactions in solution.

The rate at which the reaction changes with time depends upon its type.

Reaction Velocities

Reactions in which a molecule falls into its constituent atoms (or simpler molecules) are called monomolecular or

first-order reactions. Their velocity is proportional to the concentration x of the dissociating substance. It is a matter of simple calculus to show that the concentration $[X]_t$ existing at time t , if the original concentration at time zero was $[X]_0$, is given by

$$\ln [X]_t = \ln [X]_0 - \alpha t. \quad (1)$$

Here α is a constant appropriate to some particular reaction and temperature. Reactions in which two molecules participate to form one or more other reactions are second-order reactions. If $[A]$ and $[B]$ are the initial concentrations of the two species of molecules that disappear and X is the decrease in concentration of A after time t , then

$$\frac{1}{[A] - [B]} \ln \frac{[B]([A] - X)}{[A]([B] - X)} = \alpha t. \quad (2)$$

The process can be applied to reactions of still higher order by solving the equation

$$\frac{dx}{dt} = \alpha([A] - X)([B] - X)([C] - X) \cdots$$

Third-order reactions occasionally occur, but very few reactions of higher order proceed in a single step.

Limitations on Reaction Velocities

As in so many other cases, the foundry metallurgist's problem is not so simple as the chemist's deductions appear to make it. When we consider an actual slag reaction, an essential step in the process is the passage of, say, ferrous oxide from slag to metal and its migration in the steel bath until it meets a migrating carbon atom. It can readily be that this process is slow enough to be the governing step in determining reaction rates.

Also, if carbon is removed, CO bubbles must form against the surface tension at the gas-metal interface. The presence of roughnesses on a furnace bottom, or the introduction of a bar, may greatly facilitate the escape of gas by the same process that causes solutions to boil more steadily if

the beaker contains a few pieces of broken glass, aluminum foil, or a pointed stirring rod, all of which present points where bubbles form most easily.

Reactions in the solid state, as for example the annealing process of the malleable industry, which dissociates iron carbide into its elements, are almost completely controlled as to their rates by the ability of elements to diffuse through iron and by the ability of phases that want to separate to find nuclei, or situations where separation is easiest.

In the growth of crystals, the rate at which atoms can deposit in the necessary orderly pattern is limited and is different in different directions.

The fact that the linear crystallization velocity varies in different directions gives their regular form to crystals. The velocity is greatest in directions perpendicular to the crystal faces. The relation of crystallization velocity to temperature has been discussed in Chapter 8.

Reactions between gases and solids, as for example between CO_2 and carbon in steel, depend on the adsorption of gas on the surface and therefore are related to the character of the surface and may be influenced by the presence of other gases. Water vapor and its dissociation products are believed to favor adsorption and speed the reaction.

Plainly many factors must be considered when studying the rate at which a given reaction can proceed.

The reader may very properly ask for specific information as to the free energies of the metallurgically important substances in their several pertinent states—solid, liquid, in solution in various other substances, and so on, all in relation to temperature—or he may desire values of equilibrium constants for the important reactions, again as related to temperature, pressure, and other environmental conditions.

The field is so immense and so incompletely explored that an attempt to meet this demand is beyond the scope of this book. There are books giving those constants in this field which have been determined, in particular a series of publications by J. J. Kelley of the U. S. Bureau of Mines.

Origin and Control of Carbon in Ferrous Alloys

THERE ARE MANY better reasons for giving space to the iron-carbon alloys than the author's special interest in that field. Ferrous castings constitute an enormous proportion of the world's foundry products. Their versatility, from soft steel to hard cast iron, is due in large measure to the great effect of carbon on the properties of the metal iron, coupled with the opportunity that the allotropic changes, that is, changes in the atomic arrangement, in the metal furnish for altering the form in which carbon exists in the alloy.

Source and Concentration of Carbon

A study of the iron-carbon system must begin with some attention to the iron-carbon-oxygen equilibriums, which often determine what the carbon content of a product will be. In the upper part of the blast furnace, iron ore (typically hematite, ferric oxide, Fe_2O_3) encounters a mixture of CO and CO_2 derived from the partial attainment of equilib-

rium of atmospheric oxygen with the carbon of coke. We have already touched on the essential reaction in considering the cupola in Chapter 10.

In either the cupola or the blast furnace, air strikes incandescent coke and burns the latter. Because of the excess of coke and the high temperature, equilibrium some distance up in the furnace finally requires a high proportion of CO. As the gases ascend through the stack and impart their heat to the descending charge as sensible heat and perhaps as heat of reaction, the equilibrium will shift to higher percentages of CO_2 . However, below, say, 500°C the reaction becomes so slow that the gases retain far more CO than would be expected.

The CO- CO_2 mixtures that are in equilibrium with Fe and FeO, FeO and Fe_3O_4 , and Fe_3O_4 and Fe_2O_3 have been studied very extensively, especially by Schenck, and these equilibria, which are independent of pressure, are shown in Fig. 19-1.

Actually the line marking the equilibria of Fe and FeO marks the equilibrium of the compound FeO and Fe saturated with FeO, and in the zone above that line the oxygen content of iron decreases with CO_2 content. Shortly we shall see that iron will absorb carbon in this area if the temperature is high enough.

Returning to our blast furnace we find, in fact, gas and temperature conditions successively below the top of the

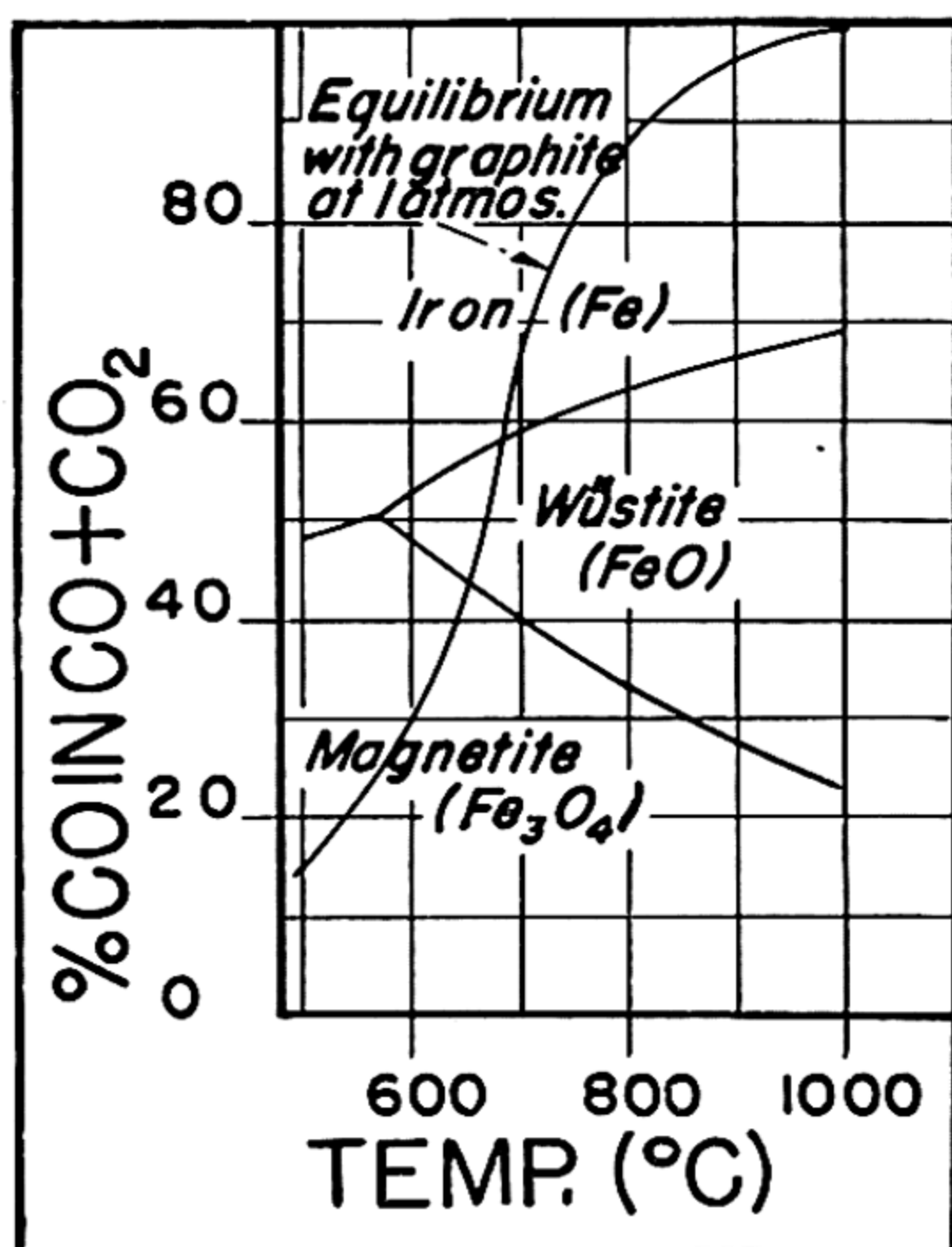
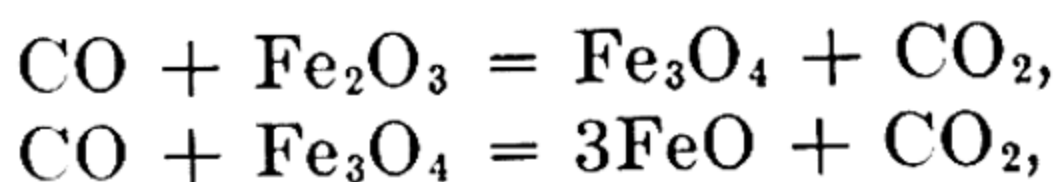
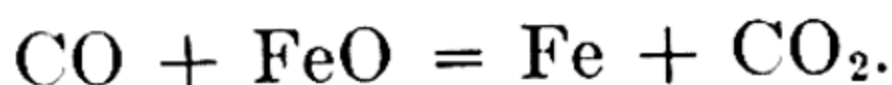


FIG. 19-1. Iron-Oxygen and Graphite-Oxygen Equilibrium. (Approximately after Kelley's data.)

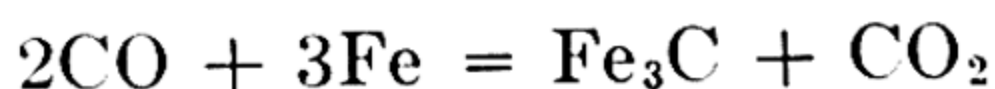
stack favoring the reactions,



and



As a result of the series, metallic iron in the solid state makes its appearance in the charge. Below the A_1 point, the reaction of C and Fe is slow, owing to a low migratory rate of carbon into iron from the surface where it might be absorbed, but above A_3 , when the iron is in the gamma state, the reaction



proceeds energetically, the carbon migrating inward into the iron particles.

The system we are considering is one of three components, Fe, C, and O, and two phases, solid and gas, when above the critical point A_1 . The solid would be of two phases below the critical point if it contained carbon. Gibbs's phase rule then teaches us that in the former case the number of degrees of freedom is

$$3 + 2 - 2 = 3.$$

That is, we can assign arbitrary values to three variables before the composition of the system is determined. If we set a pressure and temperature, two degrees of freedom are used up. If we set a ratio of CO to CO_2 , we in effect determine the carbon (or oxygen) content of the gas phase, and the composition of the gas and of the solid is completely determined. The iron will then contain a given amount of carbon. The equilibrium of CO- CO_2 mixtures with austenite of various carbon contents has been studied by several observers, and the results are summarized in Fig. 19-2.

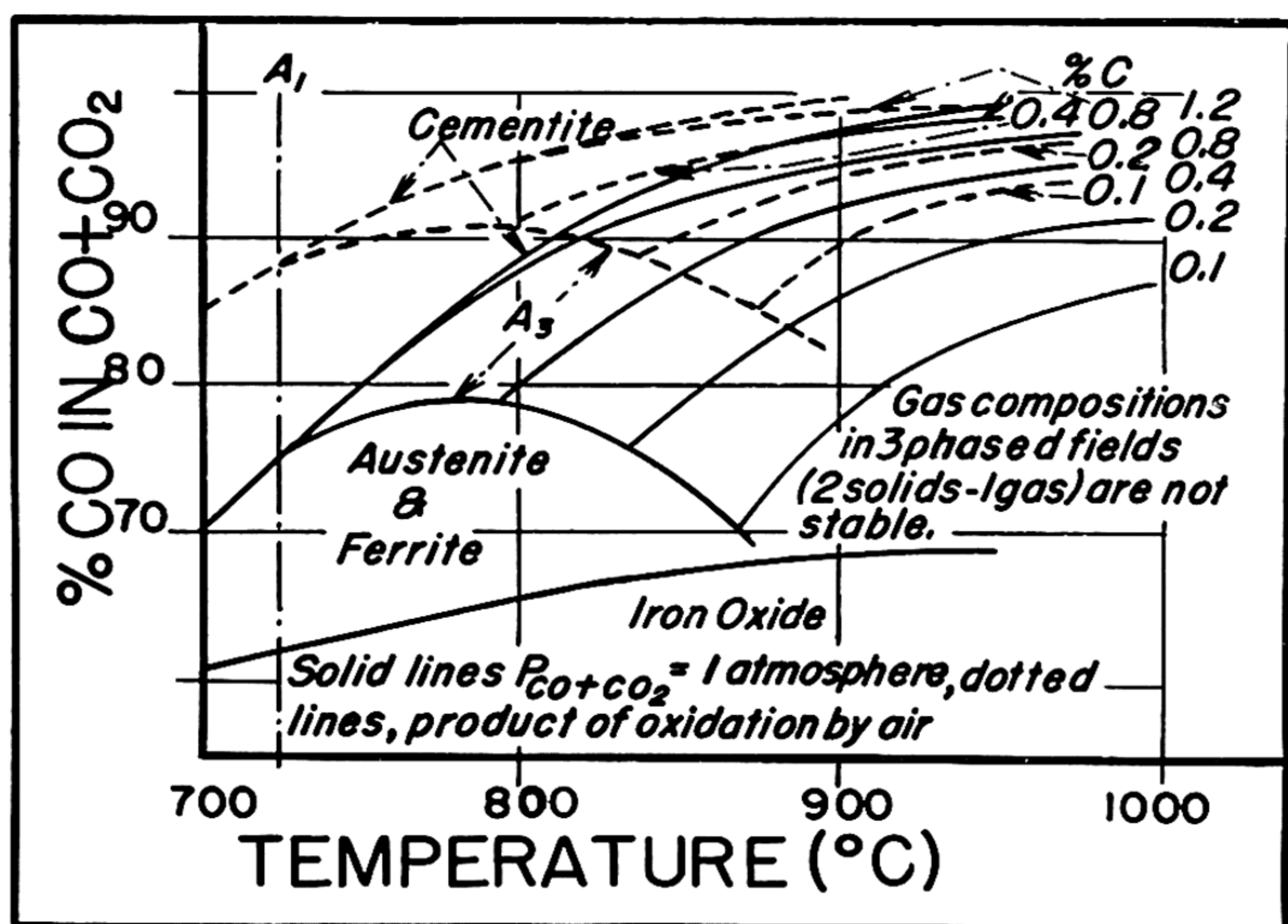


FIG. 19-2. Carbon-Oxygen-Austenite Equilibriums. (Approximately after Kelley's data.)

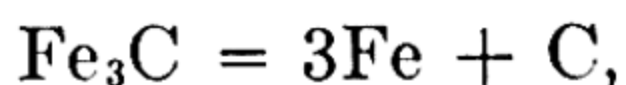
Carbon-Oxygen-Gamma Iron

Fig. 19-2 has great utility in any problem where a reaction between CO-CO₂ mixtures and solid steel is involved. Note that it is in the nature of an addition to Fig. 19-1 of this chapter, filling in data above the so-called Fe-FeO equilibrium line.

Solid iron can be carburized under the most favorable conditions up to about 1.75% C before melting. For this to occur, the CO-CO₂ mixture must be in equilibrium with cementite, and the temperature must be 1130°C, the eutectic melting point.

When the carburized iron of this or a lesser carbon content melts, the solubility for carbon suddenly increases, and—to the extent that ample contact between melt and coke exists—the carbon rises rapidly. Indeed, gases in equilibrium with coke should raise the carbon just as much.

The form in which carbon exists in liquid iron is not clearly understood. Cesaro concluded that it was present as cementite molecules, based on the form of the solidus and liquidus curves of hypoeutectoid metal. This view has now found considerable acceptance, although the possibility of dissociation, according to the reaction



cannot be excluded. For low concentrations of carbon, the ratio of atomic carbon to molecular cementite should be constant, but we do not know enough about the constants for free energy of formation of cementite dissolved in iron to set a value. For a more concentrated solution when Fe is no longer substantially constant, the proportionality of C to Fe_3C would fail, and this ratio would increase rapidly with increasing total carbon. Such a state is definitely reached in the carbon range for cast irons.

It is quite easy to reach temperatures at which the iron in contact with carbon will become hypereutectoid in composition, and indeed carbon contents above $6\frac{2}{3}\%$, that is, that of cementite, can be had without much difficulty. Just what is in solution in such cases may be left unanswered. The hypereutectoid part of the iron-carbon system, especially above the eutectic temperature, has not yet been adequately explored.

As the liquid iron from the blast furnace cools in the ladle or in pigs, the solubility of carbon decreases, and some carbon must be rejected. Actually kish, which consists of graphite flakes, floats away.

Solid Cementite-Solid Graphite-Liquid Iron

Regardless of what was in solution, it is natural that what escapes should be largely graphite. The solubility lines of cementite and graphite in solid iron would, if projected upward, intersect somewhat above 1200°C . This indicates that solid graphite and solid cementite are in equilibrium

at that temperature. One would infer, therefore, that the hypereutectic liquidus lines of the stable system should intersect at that temperature, a point not so far considered in any discussions of this region of the diagram known to the author. Above 1200°C , cementite is stable; below this, graphite.

Now solid cementite can exist at about 1200°C only in equilibrium with a saturated liquid solution in iron. Any cementite rejected above 1200°C might remain as the solid, but when cooled below that temperature it would quickly decompose into the elements. Graphite should float out. The practical result is that pig iron reduces its carbon during freezing to a value but little above the eutectic concentration.

We have not yet considered the effect of silicon, but the reader may as well be informed here as later that silicon lowers the carbon content of the eutectic so that the total carbon of pig iron is somewhat related to its silicon content.

Having now spent so much time showing how carbon enters the product of the blast furnace, we should tell the reader how all this lengthy discussion applies to the foundry.

Most cast irons are melted in the cupola, whether they are to be cast directly or subjected to a duplexing operation. Even Bessemer steel passes first through the cupola. There is some interest, and should be more, in the control of the carbon content of cupola metal. Let us see why this carbon content is not constant or solely dependent on the carbon of the charge.

Carbon Content of Cupola Metal

By the principles discussed for the blast furnace, steel scrap will gain carbon and reach the melting zone at a higher carbon content than it had when it entered the cupola. How high this carbon content will be will depend largely on the ratio of surface area to volume of the scrap used. Pig iron will find itself in an environment in the upper zone of the cupola suitable for decarburization, but being of low

ratio of surface to volume, it will not experience much decarburization. It is likely, however, to melt higher up in the cupola than steel because its melting point is lower (unless the steel has been recarburized to equilibrium).

Subsequently the mixed liquids are enriched by contact with coke, especially when accumulated in the hearth or well of the cupola. Since the time of contact is less than in the blast furnace, and the temperature lower, the recarburization seldom, if ever, reaches the eutectic concentration.

All this indicates that a cupola operating largely on pig iron will produce a product little lower in carbon than the charge, whereas one operating with light steel scrap may produce liquid metal higher in carbon than the charge. The conditions vary further with time of exposure and temperature.

Hot metal held long in the cupola hearth will strive toward higher carbons, as will steel held long below the melting point in an atmosphere rich in carbon monoxide.

Since the rate at which coke will burn, which depends on density and size of lumps, will determine how far above the tuyères melting will occur, this factor also enters into determining the carbon content.

For a given blast pressure, the rate at which the cupola will take air depends mainly on the resistance of the charge in the stack to air flow. Deep charges and charges that pack closely diminish the air intake and hence the melting rate at a given pressure. The tuyère area itself exercises little influence on the rate of input of air; hence in a given cupola the velocity of air at the tuyère is inversely proportional to tuyère area. If the blast is to penetrate well into the charge, the tuyères must be reasonably small lest the air currents merely percolate up near the cupola walls.

Shall we now visualize what happens in the cupola with respect to heat evolution and chemistry?

Much has been written in this field without greatly clarifying the subject. A major stumbling block is that

none of the reactions proceed to equilibrium. It is a waste of time, therefore, to attempt any exact quantitative calculations, and we had best confine ourselves to a qualitative description of principles.

In intent at least, a cupola while operating does not change in temperature at any given level. Therefore, the heat evolved by burning in any thin layer is exactly balanced by the heat carried downward in the form of increased temperature by metal and unburned fuel that carried upward by the increased heat content of the gaseous products of combustion, and that lost through the walls. For the sake of illustration, we may confine our thoughts to a unit area near the center of a large cupola and so eliminate the wall loss from our discussion.

The several gains and losses of heat, even with this simplification, are not predictable. The amount of coke burned in unit time and the heat evolved per unit of weight depend on the gas composition, on the area of coke-gas interface, and on the temperature. The amount of unburned coke passing downward depends on the rate at which coke in and below the layer being considered burns.

The amount of heat passing into the iron depends on the surface exposed and on the temperature. The increase in the heat content of the gas in passing through the layer is that liberated by fuel burning, less that absorbed by descending fuel and metal, and therefore is related to the iron-coke ratio of the charge. The temperature of the layer is the integration of all these variables from the tuyère level to the level being studied, all the heat changes being multiplied by the appropriate specific heats.

One might set up differential equations expressing all those conditions and at best he would be confronted still by the uncertainties attending the approach to equilibrium made by the gas composition.

Air is blown into the bottom of the cupola against glowing coke. Since it takes time for oxygen to combine with solid

carbon, there will be an appreciable distance above the tuyères where free oxygen exists, and in this region the products of combustion will approximate those derived from the reaction



As the temperature rises the reaction goes more and more completely to the right. Thus without any reaction between CO_2 and C, the ratio of CO to CO_2 increases, and the heat evolved per unit of oxygen used up grows less and less. Also as time goes on, that is, as the gas rises in the cupola, the free oxygen decreases, requiring more and more CO in relation to CO_2 for equilibrium, at a given temperature.

When the oxygen is exhausted, or nearly so, the gas will tend toward equilibrium with carbon in the reaction



This reaction at temperatures near the melting point of iron will go practically to the complete formation of CO at equilibrium. It is unlikely, however, that the time of contact with carbon will be sufficient to attain this end, and statements are made that instead of 100% CO only 15% or 20% CO may be formed in the melting zone.

Of course the combustion of C by CO_2 as has been described absorbs heat instead of liberating it. We have seen in our discussion of combustion how the maximum temperature is reached before all CO is burned to CO_2 . Furthermore, the maximum temperature is decreased by the transfer of heat to the melting iron, which depends on the iron-coke ratio and the amount of heat the iron has picked up in descending to the observational zone.

As the gases ascend into progressively cooler levels, the composition in equilibrium shifts toward the formation of CO_2 and soot, and this is facilitated by the catalytic action of the iron surface. The reaction is probably faster than when it proceeds in the opposite direction, for it is less related to a time during which carbon and gas must remain

in contact. The soot, if deposited, descends again toward the melting zone and if it encounters CO_2 or free oxygen, is reburned.

It is important to note that, except as affected by changes in time of contact of gas and fuel, the rate of input of air into a cupola determines the rate at which heat is generated. Coke must be fed in at exactly the rate at which it is burned. If it is put in too slowly, that is, if it burns away faster than it is put in, the level of the coke bed will drop continuously. It is impossible to put it in too fast, for there will be no room for it. To this extent the cupola is self regulating.

The rate at which iron is melted depends on the iron-coke ratio of the charge. Since the cupola virtually determines its own flue-gas composition, a pound of coke will liberate a given number of heat units. This will be just sufficient to melt and to superheat to a given extent a particular number of pounds of iron. If less iron than this is charged per pound of coke, a given charge of iron will be delayed in reaching the melting zone until the excess amount of coke has burned away. Actually, the melting zone will rise somewhat under these conditions, owing to the preheating action of this excess coke on the charge above, and liquid iron will have more time to superheat in flowing to the well. If more iron is charged than the coke can melt, solid iron will finally reach the cupola well.

Although the cupola is a very simple-looking object, the reader has no doubt realized that its chemistry and thermal engineering are quite complicated. This, no doubt, accounts for the violent differences of opinion existing in the field of cupola operation.

In so complex a subject, our conclusions may be clarified by certain practical observations. It has been actually found by tests on a large-scale operation that the carbon content of the charge affects that of the product, but the latter is more uniform than the former. Fast driving of a cupola, accompanied by a somewhat lower coke to iron

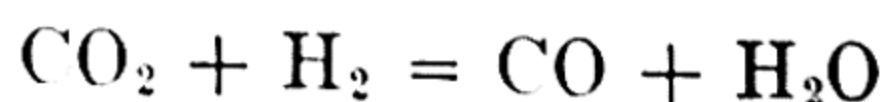
ratio, reduces the carbon content of the cupola product. Coke that breaks up fine usually produces a lower carbon, perhaps because the increased surface produces a thinner melting zone. Coke having a high kindling temperature produces high-carbon metal, perhaps by prolonging the time of contact of liquid iron with coke.

Since the steelmaking reactions were discussed in Chapter 17 as examples of decarburization, we may dismiss the melting processes involving deliberate decarburization with only a few words.

Cast irons, and more frequently malleable iron, may be melted in reverberatory furnaces charged either with solid melting stock or, especially in the latter case, with molten cupola metal.

Chemistry of the Reverberatory Furnace

Reverberatory furnaces were originally hand fired. Coal was burned, with forced draft, using a thick enough bed and so little air that the products of combustion resembled producer gas in being rich in CO. Additional air was supplied by a top blast admitted to the furnace just beyond where the products of combustion entered the hearth. The amount of this top blast was so regulated that the gases escaping from the furnace would contain around 1% O₂, perhaps 3% or 4% CO, and the remainder of the oxygen as CO₂. Such a composition can be approximately reconciled to dissociation of CO₂, which should yield twice as much CO as O₂. At present, coal is usually burned in the pulverized state, but the gas composition is still similar. Incidentally, tests have shown that the ratio of hydrogen to water vapor arising from the hydrogen and moisture in the coal adjusts itself well to the CO-CO₂ ratio found in the gas. Indeed, it is probably more accurate to calculate the H₂-H₂O ratio from the equilibrium constant of the reaction



than to attempt an analysis under operating conditions, in view of the small amount of H_2 encountered.

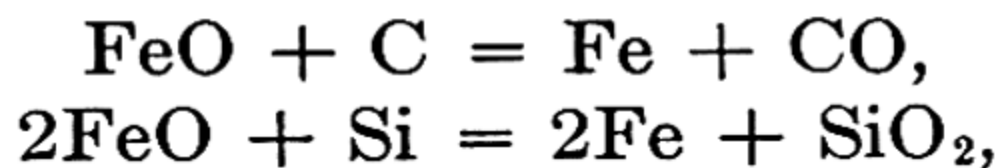
Gases of this composition are obviously in equilibrium with iron oxides of higher order. Especially below about $700^\circ C$, when FeO is unstable, Fe_3O_4 being the lowest oxide found, the solid charge suffers considerable surface oxidation. The oxides melt and if they touch a silicious lining, they are converted into complexes of FeO , Fe_2O_3 , and SiO_2 . Carbon is removed at a rate limited by its migration in the solid iron, and since Si and Mn do not diffuse readily, they are not much oxidized in the solid.

When the charge is melted, and especially before the slag is removed, all three of these elements are oxidized by reaction with FeO transferred to the iron from the slag and by Fe_2O_3 , which is insoluble, or unstable, in iron and reacts only at the slag surface. After the removal of slag, oxidation proceeds at a rate determined by the speed with which oxidizable elements reach the surface by diffusion or convection. These rates cannot well be measured but they are not fast, and except in thin baths, changes in composition are slow. In open-hearth furnaces the rate of carbon elimination is consistent with the idea that it is controlled by a migratory phenomenon.

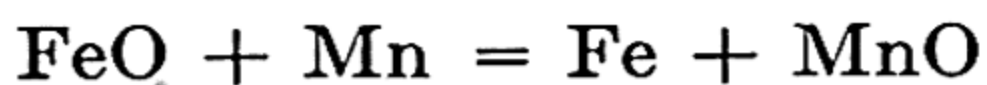
Decarburization in the Converter

Decarburization in the Bessemer converter is peculiar in that the metal itself comes into intimate contact with atmospheric oxygen. It is thus saturated with FeO , which oxidizes silicon and manganese, and also the oxygen itself reacts directly.

The reaction constants for



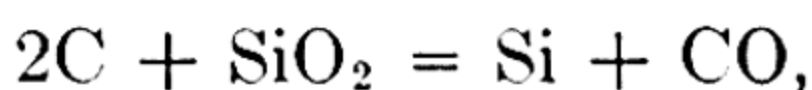
and



are such that at the initial converter temperature Si and Mn must be reduced to trivial concentrations before an FeO content is attained that will permit the oxidation of carbon, even from the molten cast iron with which the converter is charged.

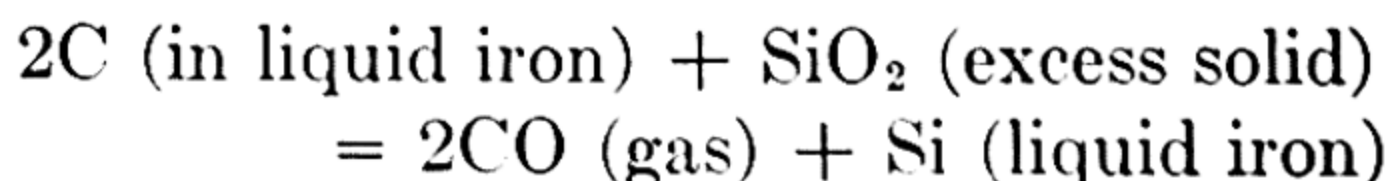
Reduction of SiO_2 by C

At very high temperatures these reaction constants so change that the reaction



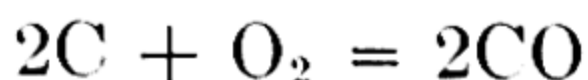
which goes to the left near the melting point of commercial irons, changes direction and proceeds to the right at electric furnace temperatures, permitting the reduction of Si from silicious slags into steel by carbon in electric furnace practice and also the manufacture of ferrosilicon.

The reaction

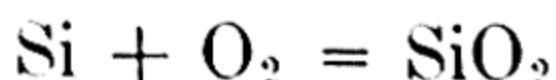


is of some interest as typical of the preferential oxidation of one element or another in liquid iron.

The reactions



and



have been studied.

Calling these reaction constants K_1 and K_2 , respectively, it has been found that

$$\log K_1 = \frac{10660}{T} + 6.316; \quad (1)$$

$$\log K_2 = \frac{31200}{T} - 4.57; \quad (2)$$

$$K_1 = \frac{P_{\text{CO}}^2}{[\text{C}]^2 P_{\text{O}_2}} \quad \text{and} \quad P_{\text{O}_2} = \frac{P_{\text{CO}}^2}{[\text{C}]^2 K_1}; \quad (3)$$

$$K_2 = \frac{1}{[\text{Si}] P_{\text{O}_2}} \quad \text{and} \quad P_{\text{O}_2} = \frac{1}{[\text{Si}] K_2}. \quad (4)$$

Equating the two values of P_{O_2} and rearranging, we have

$$\frac{P_{CO}^2[Si]}{[C]^2} = \frac{K_1}{K_2} = K_3. \quad (5)$$

From Equations (1) and (2)

$$\begin{aligned} \log K_3 &= \log K_1 - \log K_2 \\ &= -\frac{20540}{T} + 10.886. \end{aligned} \quad (6)$$

As the absolute temperature T rises, the fraction decreases and $\log K_3$ and hence K_3 increases; hence with rising temperature $P_{CO}^2[Si]/[C]^2$ increases.

For a constant partial pressure of CO, therefore, the silicon concentration in equilibrium with a given carbon (both dissolved in iron) rises. At room pressure, $P_{CO} = 1$, and that term drops out. If a large excess of C is present and the temperature is high enough to melt iron, the activity of carbon dissolved in iron is equal to the activity of carbon itself, and C can be treated as an excess phase and its concentration disregarded, an increase in silicon with temperature being indicated under these conditions.

There is a slight inconsistency in the foregoing discussion, for Equation (2) should have been written for liquid SiO_2 , not solid, at the temperature at which a furnace lining of SiO_2 begins to melt.

If no excess of carbon is present, the reaction with oxygen in liquid alloys of iron, carbon, and silicon will proceed in the direction that will cause approach toward the establishment of the equilibrium conditions represented by K_3 .

Microstructure of Iron-Carbon Alloys

THE STRUCTURAL CHANGES that occur in iron-carbon alloys during freezing and further cooling are of predominant importance. They are best considered in terms of the iron-carbon constitutional diagram, although many of the changes require the presence of other alloys for their practical consummation.

In the next chapter we shall give some consideration to the effect of such alloys on the constitutional diagram. For the moment it suffices to point out that an alloy system containing more than two components cannot be represented in two dimensions, that is, on a flat surface.

The Iron-Carbon Diagram

Probably all readers of this book already have a general familiarity with the iron-carbon diagram. Many may have regarded it as some sort of map, based purely on experiment, on which the areas, as to temperature and composition, in which various phases are in equilibrium, have been marked out. Actually it is much more. The boundaries are located where they are as expressions of the solubility

relations represented in most general form by the van Laar equation,

$$\ln \frac{X_{A_1}}{X_{A_2}} = \frac{L_{tA}}{R} \left(\frac{1}{T} - \frac{1}{T_{tA}} \right), \quad (1)$$

which says that the natural logarithm of the ratio of the molar concentrations of a solvent A in two phases, 1 and 2, is equal to the latent heat change when pure A passes from state 1 to state 2 times the difference of the reciprocals of the absolute temperature of observation and of the transformation of pure A.

We have previously encountered this equation as Equation (4) in Chapter 7. The change of sign within the parentheses is due to the fact that in the earlier chapter the latent heat of fusion is the change from state 2 to state 1, whereas in Equation (1) of this chapter the change is from 1 to 2 and therefore involves a reversal of sign.

The only uncertainties in the application of van Laar's (or Schroeder's) equation rise out of uncertainties in our knowledge of the thermal constants, which change with temperature, and of the state of molecular aggregation of the constituents in a solution, and possibly of varying activity coefficients.

Need the reader be reminded that in this, as in all other binary diagrams, no vertical boundaries exist unless complete insolubility of the corresponding phases is admitted, a condition probably sometimes approached? Horizontal boundaries separate two two-phased fields having 1 phase in common. Two-phased fields are separated from single-phased fields by inclined lines, and reading horizontally across the diagram, we find that two-phased and single-phased fields alternate, the latter phase being common also to both two-phased fields that adjoin it. A single-phased field can touch a field of two other phases only at a point on a horizontal boundary of the two-phased field. All this is the result of phase-rule considerations.

It happens that the iron-cementite system, though metastable, transforms so slowly that there is no difficulty in reproducing its constitutional diagram. Under suitable conditions, however, the stable iron-graphite state is obtained. Since both systems have operating importance,

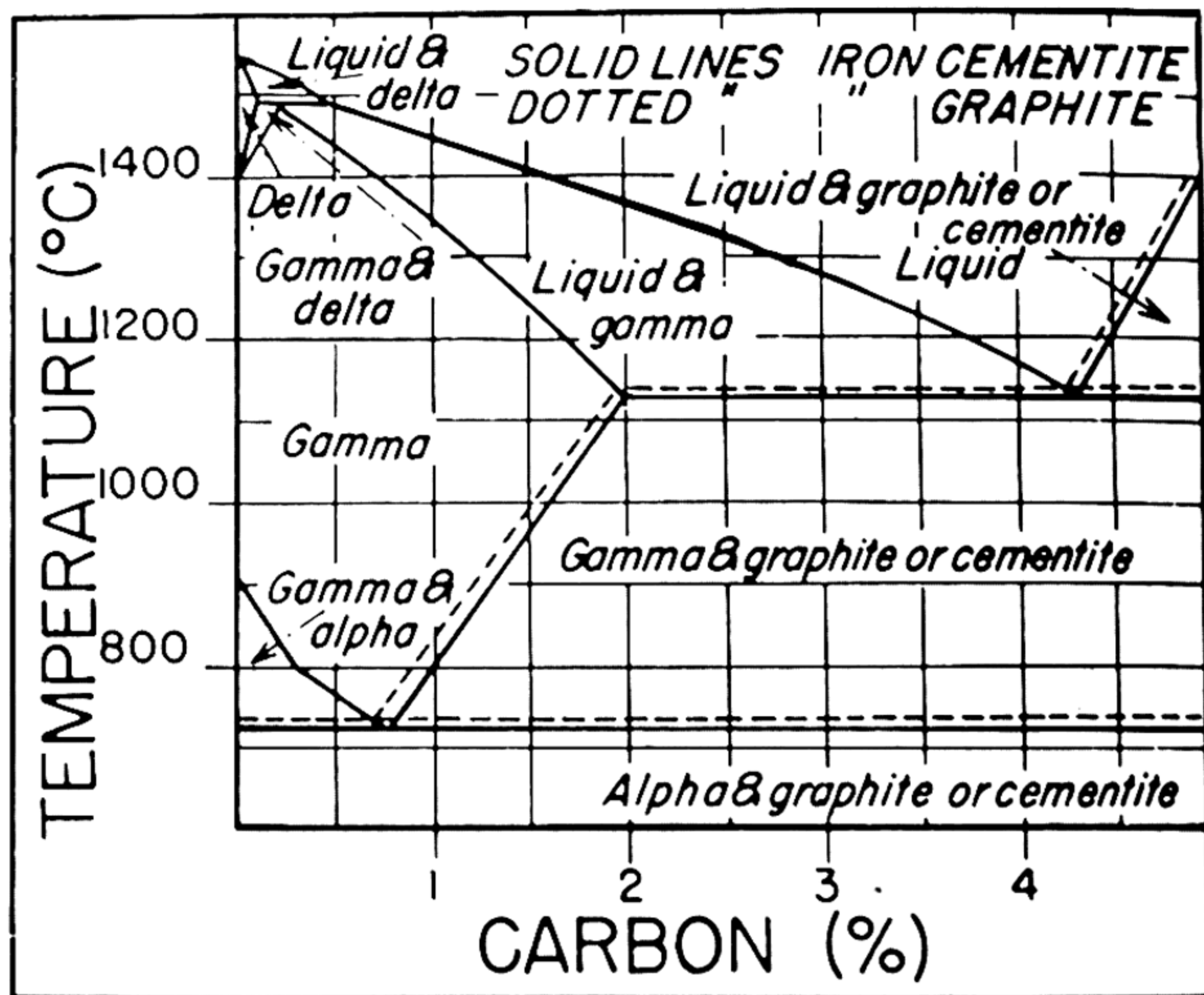


FIG. 20-1. Iron-Carbon Equilibrium. (Based on Metals Handbook.)

it has become customary to show both on a single diagram by solid and dotted lines, respectively.

Leaving aside the usual transformations as probably already familiar, there still remain phenomena (related less to structural characteristics than to the distribution and form of the phases) that require the foundryman's attention.

Low-Carbon Steels

First, we deal briefly with cast steel. In the liquid state it is probable that the metal is a solution of cementite, perhaps slightly dissociated, in iron. Any steel below 0.55% C begins to freeze by the separation of δ or body-centered

iron containing a little carbon, never over 0.08%. These crystals are unstable below 1492°C and in steels of over 0.18% C they change to face-centered iron containing 0.18% C. As the temperature falls, the carbon content of both solid and liquid increases and the amount of liquid decreases, until at the solidus presumably there is no liquid and the solid has the carbon content of the steel.

Actually this state of affairs exists during very slow freezing but not when freezing is more rapid. The face-centered iron that freezes out appears in dendrites or branches, forming a skeleton of a complete crystal. That first deposited is relatively low in carbon. The diagram supposes that when richer layers are deposited on their thread-like axes, carbon will diffuse inward to equalize the concentration. Actually this seldom happens, so that the solid metal has a lower average carbon content than that corresponding to the solidus line which bounds the field of solid-liquid equilibrium on the low carbon side. There is thus at any given moment more liquid in proportion to solid than the diagram would warrant on the assumption that the relative amounts of solid and liquid are proportional to the differences between the alloy's composition and the solid and liquid phases, respectively (lever principle).

The Nonmetallic Phases

This effect is more pronounced in thin-walled castings than in heavy sections or ingots. Any nonmetallic phases, liquid or solid, such as the Mn-Fe-S-O complexes discussed in Chapter 17, are crowded to the boundaries of the growing crystallites, where they finally lodge when freezing is complete. Their pattern, both as to location and form, whether films, chains, or isolated spherulites or crystals, is then determined for all time and nothing can be done about it. In ingot practice they will be subsequently broken up by rolling, but in castings they stay put; hence the importance of suitable deoxidation practices in the foundry.

The freezing grain size is then determined, representing the size of dendrites in the steel. On cooling below the A_3 line, nuclei of body-centered alpha iron again appear, and the alloy is converted into ferrite and austenite. The latter decreases in amount and increases in carbon concentration as the temperature falls until at 723°C it contains about 0.85% C. Below that temperature the austenite areas break up into pearlite.

Purpose of Normalizing

The structure then consists, as in Fig. 20-2, of a relatively coarse Widmanstätten pattern of ferrite and pearlite,



FIG. 20-2. Medium Carbon Steel, as Cast. $100\times$; Nital Etch.

which, because of the planes of weakness along the ferrite planes, is not particularly desirable. These planes were probably cleavage planes in the gamma iron crystals. On reheating into the gamma iron field, the alloy again becomes homogeneous but establishes a system of smaller gamma

iron crystals having, according to Hawkes, no discernible relation to the crystal size on freezing. When this austenite is allowed to cool, the ferrite is largely rejected toward the boundaries of the new austenite grains, and the final pattern consists of pearlite islands randomly dispersed in ferrite, as in Fig. 20-3. Be it understood that the heat treatment,

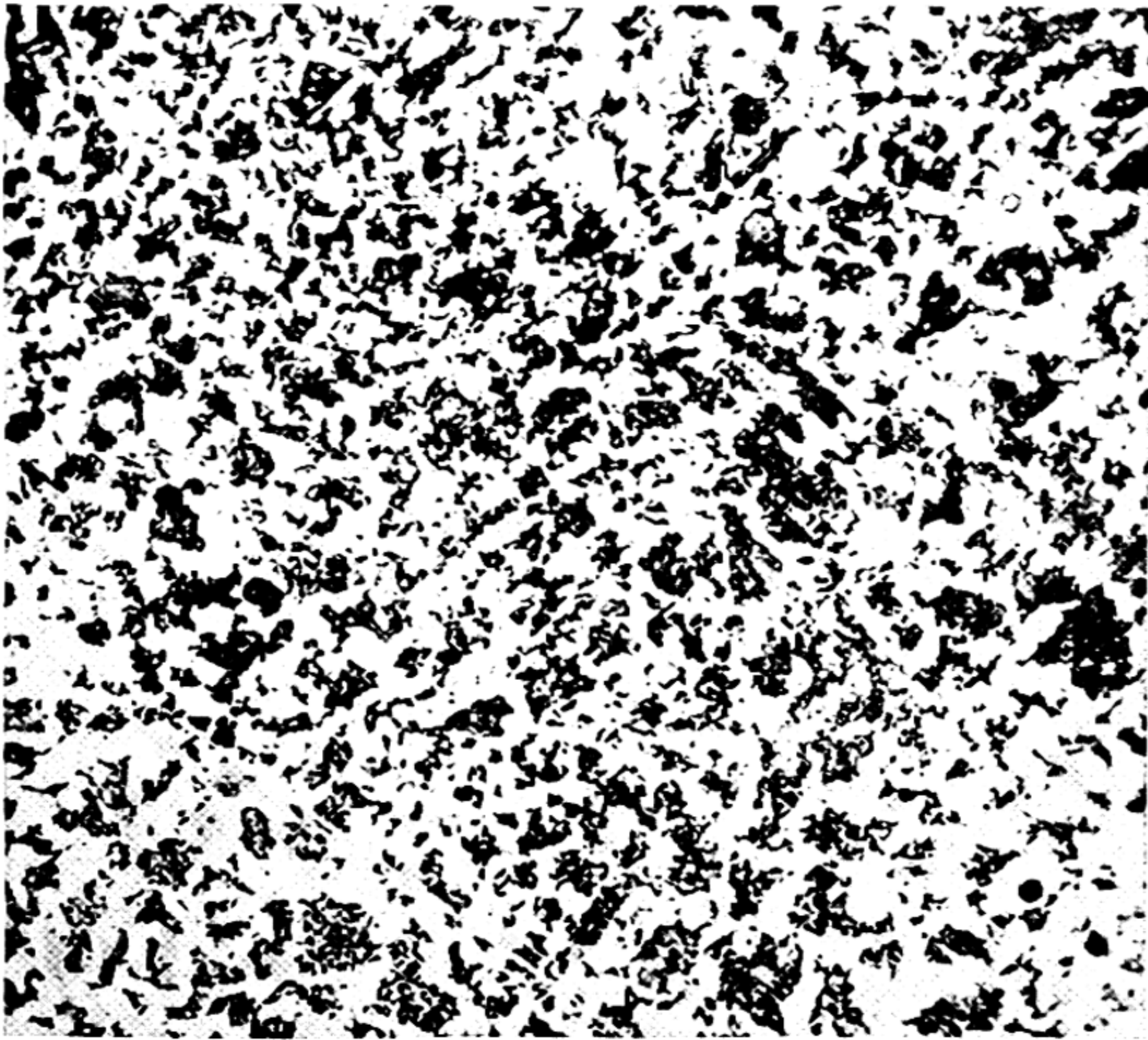


FIG. 20-3. Medium Carbon Steel, Normalized. 100 \times ; Nital Etch.

normalizing, was not intended to alter the final phases present but only their distribution. The phase diagram does not cover the point at all but does tell us at what temperature to work.

Freezing of Cast Irons

The freezing of the gray cast irons is a much more complex and, therefore, very interesting process. It has been studied particularly by Boyles, who advanced the following conception of the process. The explanation is here reduced to a discussion of the iron-carbon system, although the

realization of some of the assumptions requires the presence of other elements.

As in the case of all hypoeutectic alloys (less than 4.3% C in the absence of other alloying constituents) freezing of gray cast irons begins by the building of a dendritic pattern of solid austenite forming the skeleton axes of potential crystallites. When the temperature has fallen to the eutectic melting point, these interlacing branches fill out nearly the whole of the volume occupied by the metal, but there are large voids between the branches comprising still liquid metal having at equilibrium a carbon concentration of 4.3%. If no graphite forms, that is, if white cast iron results, this freezes, breaking up in the process into more austenite and cementite. It may well be emphasized at this point that the so-called cementite that freezes may not have the composition Fe_3C but may be of lower carbon content.

Cementite is characterized by a certain arrangement of iron atoms in space, carbon atoms being present interstitially between them. Usually, and especially at room temperature, there are one-third as many carbon atoms as iron atoms, but at higher temperatures either fewer or more carbon atoms may exist in the lattice without causing its collapse.

If the cementite is sufficiently unstable or the time at temperature long enough, the freezing of the eutectic will proceed toward the stable system rather than toward the metastable system. It begins by the separation of graphite from austenite (we refrain here from any discussion of the possible differences between stable and metastable solutions) at centers of crystallization having no particular relation to the pattern of the austenite dendrites.

What separates out in freezing is a mixture of graphite and austenite. From a graphite aggregate, a flake of that material will tend to grow out radially with an austenite layer on each side. Actually there will be many flakes in

many planes, which, with their adjacent austenite, form solid spheroids.

Inclusions and segregating elements are forced into the remaining liquid.

Of course when graphite encounters a solidified dendrite of austenite, it has to quit growing or divert its path around the solid. Graphite grows in planes, or flakes, or scales, or whatever one wishes to call them, for two possible reasons. First, so long as the edge of a flake makes contact with liquid eutectic, carbon can reach there more rapidly than by migration through an austenite layer; and second, the linear rate of growth of crystals is anisotropic, that is, growth along the several crystallographic axes is at different rates. This difference accounts for the exterior form of crystals. In graphite that crystallizes, if it can, as a hexagonal plate, the rate of growth in the plane of the plate, in the three directions at right angles to the sides of a hexagon, is much faster than in the fourth crystallographic axis at right angles to the plane of the hexagon.

A given flake must cease to grow when its advancing edge no longer receives graphite. If the decomposition of cementite in the liquid is slow, austenite may freeze around the edge of a flake and stop, or nearly so, its growth. Crystallization must then start elsewhere, or perhaps the metastable eutectic will begin to freeze, making mottled cast iron.

Effect of Sonims on Graphite Formation

An interesting viewpoint on the freezing of hypoeutectic alloys, whether they freeze in the stable or metastable system, is due to DeSy. In order that a eutectic may freeze, two phases must crystallize at the same time. Supercooling might be determined by the rate at which the new phase can crystallize.

Inclusions, which like silica are hexagonal in crystal habit and hence similar to graphite, would favor the

separation of a graphite-solid solution eutectic, whereas silicates of orthorhombic habit (rectangular prisms) would favor the separation of cementite. By such a mechanism, sonims, acting as spores, might determine what system was formed on cooling.

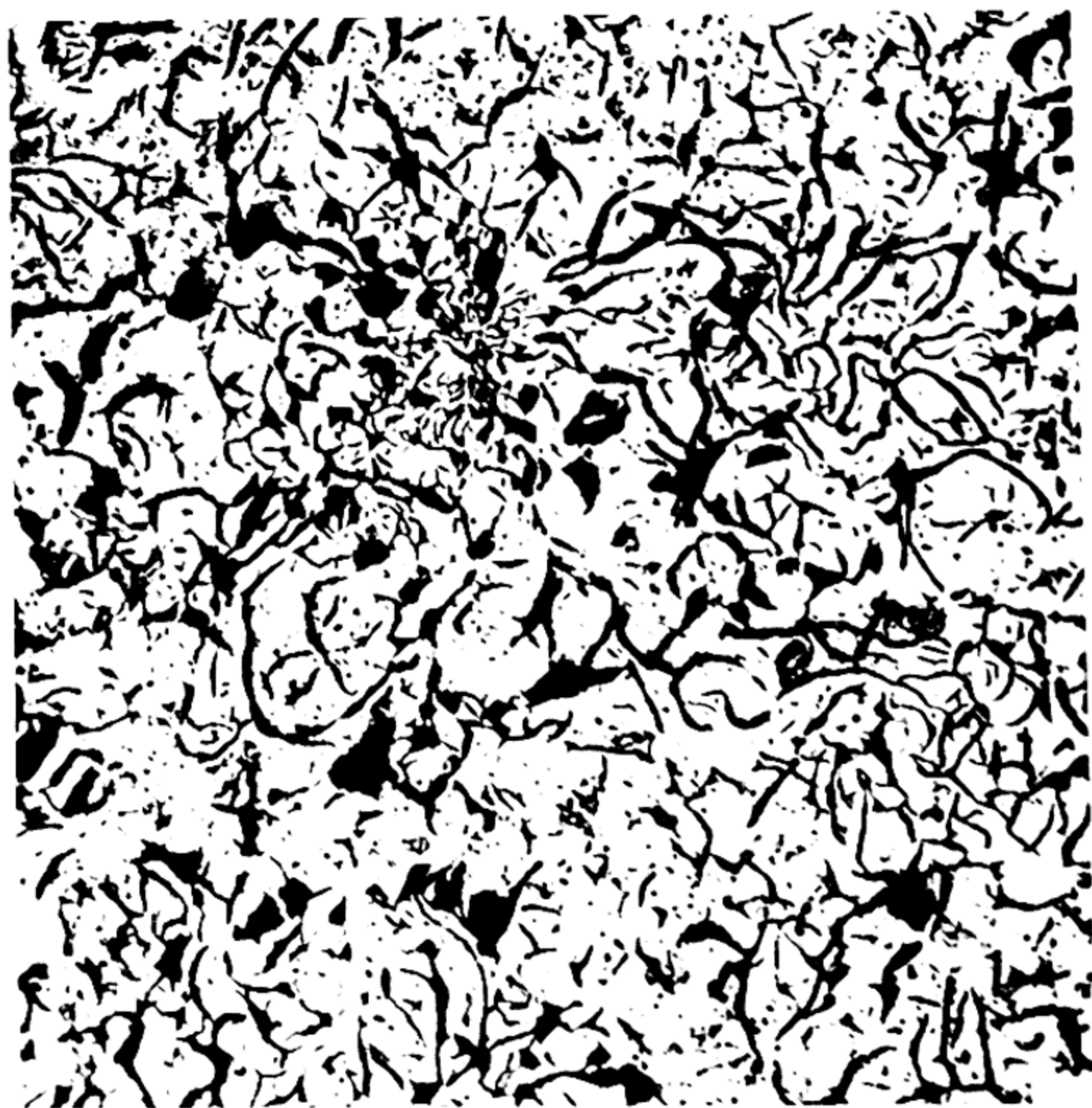


FIG. 20-4. Rosette Distribution of Graphite Flakes in Gray Iron. 100X; Unetched.

Morrogh and his associates have found that cerium added to low-sulphur hypereutectoid irons may cause the graphite to separate as spherulites, such as those to be discussed later and having forms similar to those shown in Fig. 20-11.

If an iron graphitizes very easily, that is rapidly, from numerous centers of crystallization, plainly the length of the flakes will be small by the time adjacent freezing spheroids touch. Also slow graphitization may make small flakes by the mechanism of sealing the ends of the flakes as already described. Thus the longest flakes will correspond to some intermediate rate of graphitization, and the size of flakes

will depend on the rate of abstraction of heat, the linear crystallization velocity of graphite (which should be rather constant as described at the end of Chapter 8), and the graphitizability of the alloy, which in turn is determined by

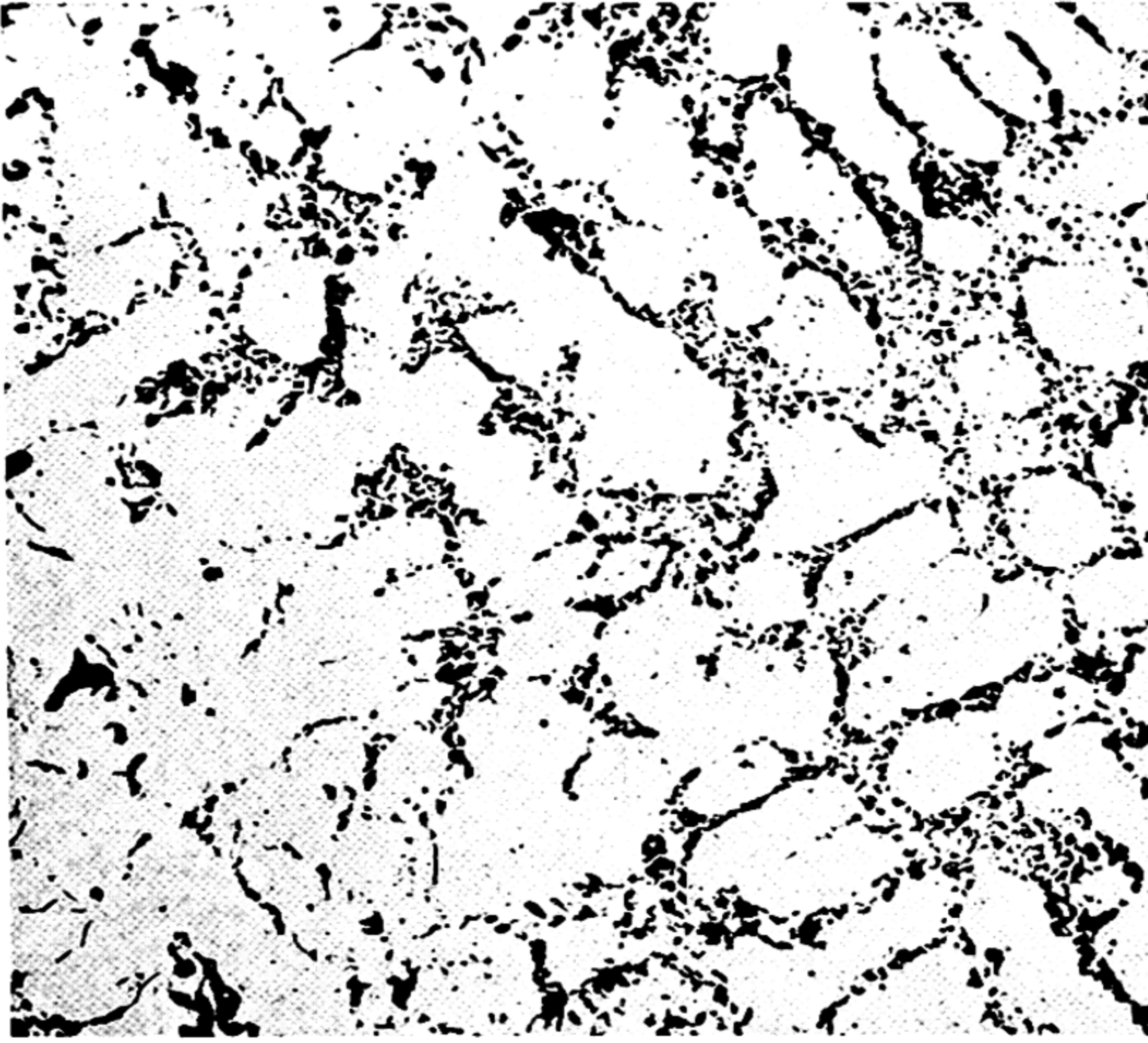


FIG. 20-5. Lacy, Eutectic-Like Graphite in Gray Iron. 100 \times ; Unetched.

the composition of the metal with regard not only to the commonly considered elements but perhaps to many others.

Supercooling and Graphite Form

Schneidewind and d'Amico related the form of graphite to the degree of supercooling, that is, to the temperature at which it grows. At or near the eutectic freezing point, the normal, rosettelike form called by the Japanese a chrysanthemum-like (kekume) structure, forms (Fig. 20-4). At a temperature some 50°C below the eutectic melting point, the lacy eutectic graphite precipitates (Fig. 20-5). For still greater supercooling, the iron will freeze completely

white, that is, by the deposition of cementite and austenite (Fig. 20-6). The presence of a third element, producing a eutectic freezing range, favors the formation of graphite from the liquid.

Graphitization in Solid White Cast Iron

These white iron castings, when caused to graphitize by suitable heat treatment, form the malleable iron of com-

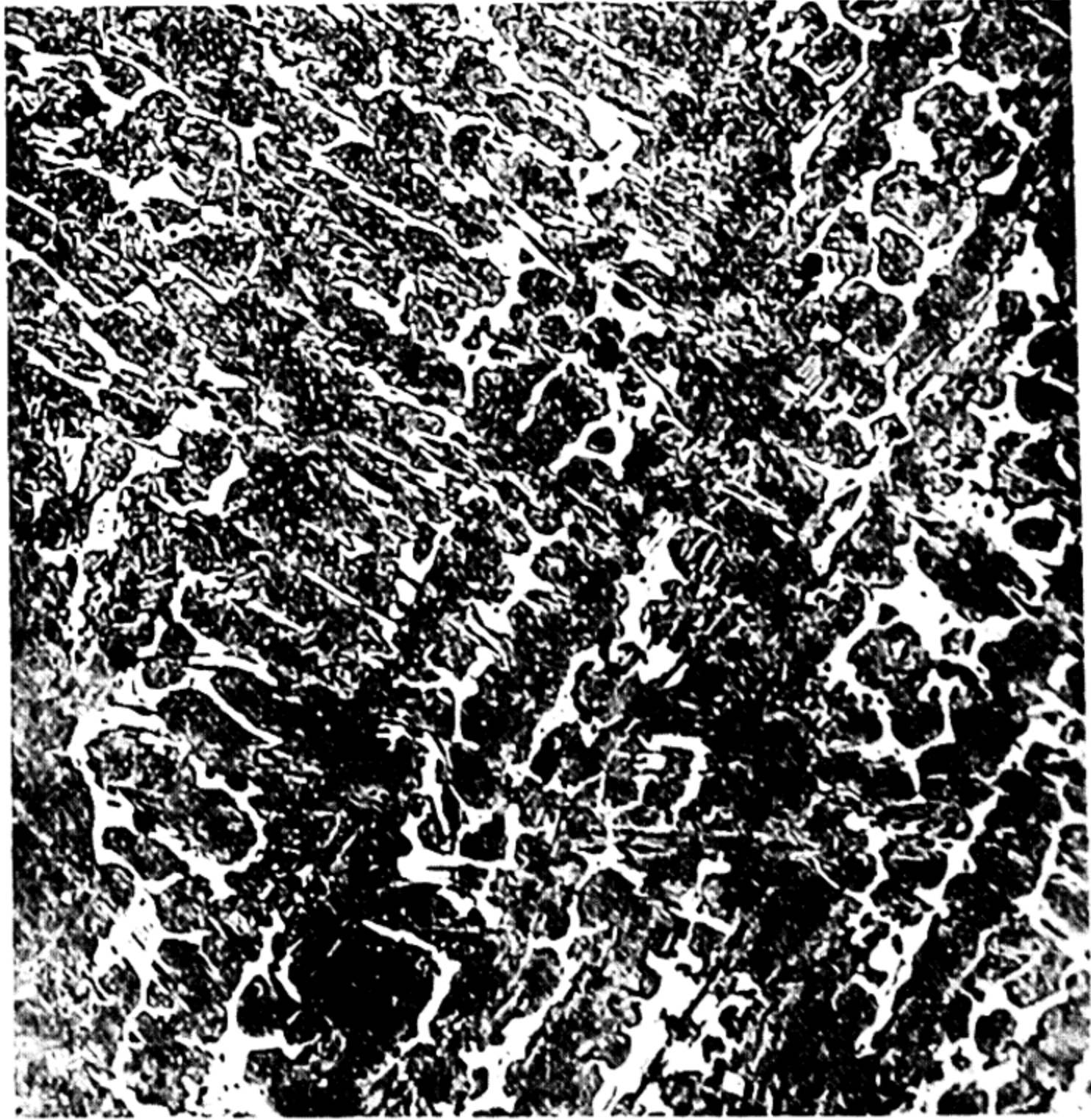


FIG. 20-6. White Cast Iron. 100 \times ; Nital Etch.

merce. When such an iron is heated to a temperature of, say, 950°C, graphite nodules form at the boundary between cementite and austenite (Fig. 20-7). It is quite likely that the particular point on the boundary is one to which a sulphide particle or other impurity is rejected. Lately there has been some suggestion that the number of nodules forming in the range 400°C-600°C is greater than if their growth is started at higher temperatures above A_1 .

At such a temperature the double iron-carbon diagram

indicates that the solution in equilibrium with cementite is richer in carbon than that in equilibrium with graphite. Therefore, austenite having the former concentration will crystallize carbon out onto a graphite particle and be enabled to dissolve cementite. By a repetition of this

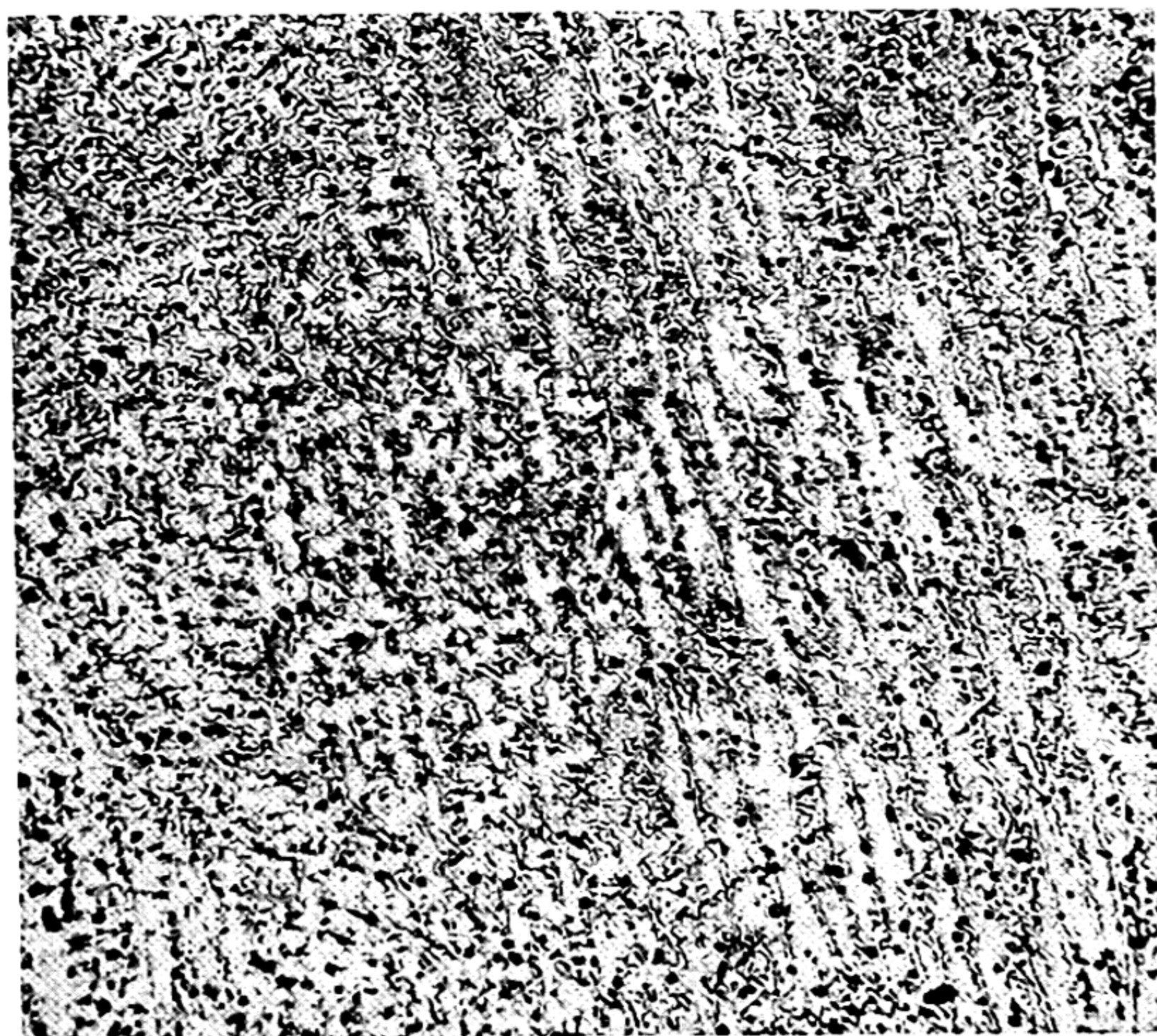


FIG. 20-7. Appearance of Temper Carbon at Cementite-Austenite Grain Boundaries. 30 \times ; Light Nital Etch.

process, an approximately spherical area around each carbon nodule becomes robbed of all its cementite, and this spheroid grows with time until there is only solid solution and graphite. The carbon content of the former is that corresponding to the austenite-graphite equilibrium shown by the gamma graphite equilibrium of the diagram, Fig. 20-1.

One should note that as this process proceeds the electrical resistance first falls to a minimum, when cementite has disappeared, and then rises sharply, which suggests strongly a difference, in kind, of the solution. Also, the X-ray spectrum of the (hot) solid solution in equilibrium

with graphite is indicative of an unaltered space lattice of gamma iron, whereas that in equilibrium with cementite is expanded, as expected, by the substitutional carbon atoms. The author is disposed to regard these facts as evidence of difference, in kind, of the stable and metastable solution, although he does not wish to insist on any particular

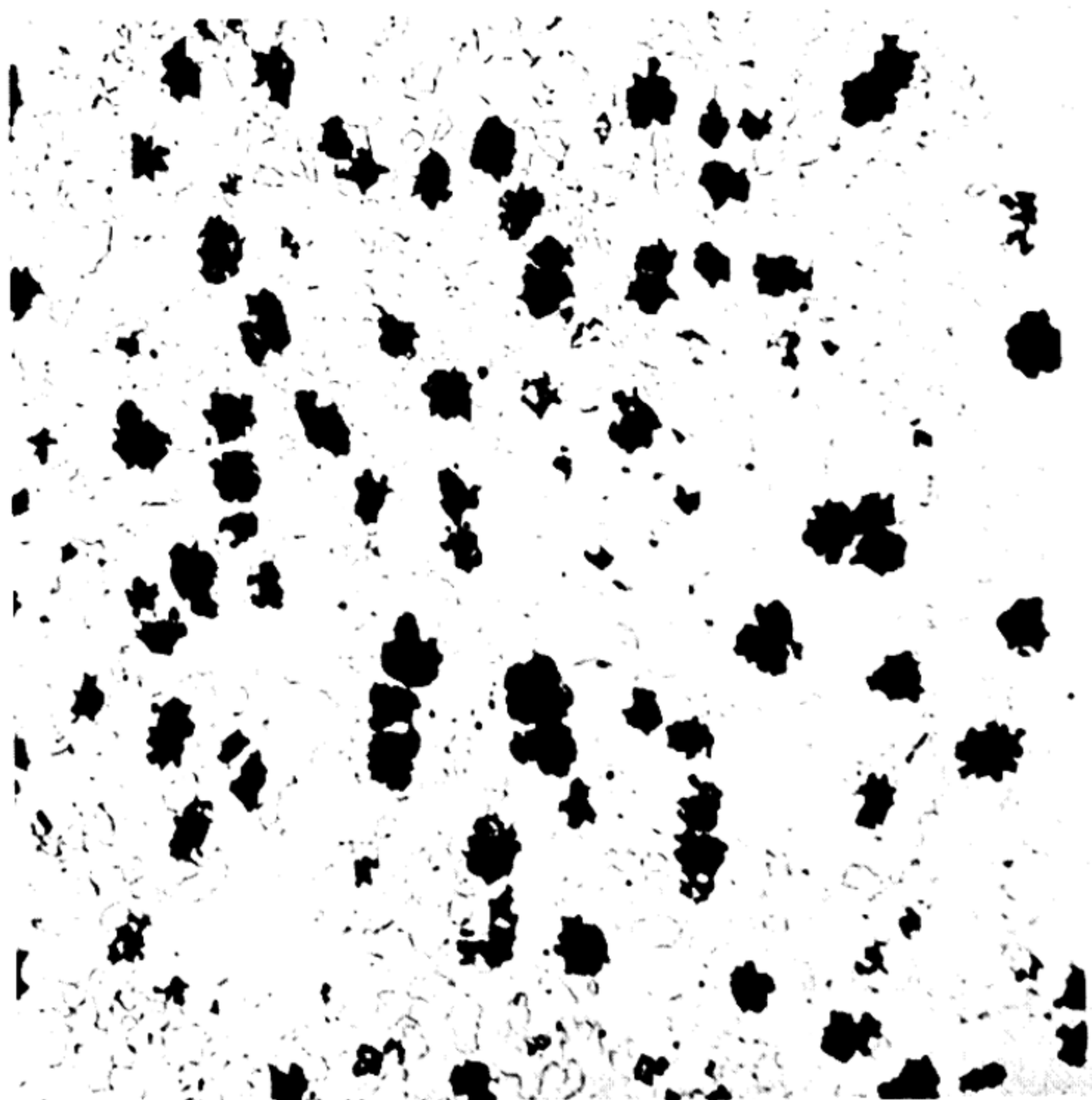


FIG. 20-8. Well-Formed Temper Carbon in Malleable Iron (Annealed at Low Temperature). 100 \times ; Nital Etch.

explanation of the kind of difference. He has referred to the stable type as boydenite.

As the temperature is lowered, more and more graphite is deposited until we reach A_1 . Here there is a narrow range of temperature, between A_1 stable and metastable, in which the equilibrium is either cementite-austenite or ferrite-graphite; consequently austenite that may form by further cooling can be converted directly to the stable state. Graphitization here is about ten times as rapid as immediately above, and one hundred times as rapid as immediately

below, this range. If we pass below A_1 metastable fast enough, pearlitic cementite must be graphitized by a process similar to that in the gamma iron range, which is, however, very slow, owing to the small concentration gradient between ferrite saturated toward graphite and cementite and to the limited solubility of carbon in ferrite. The final product is malleable iron (Fig. 20-8).

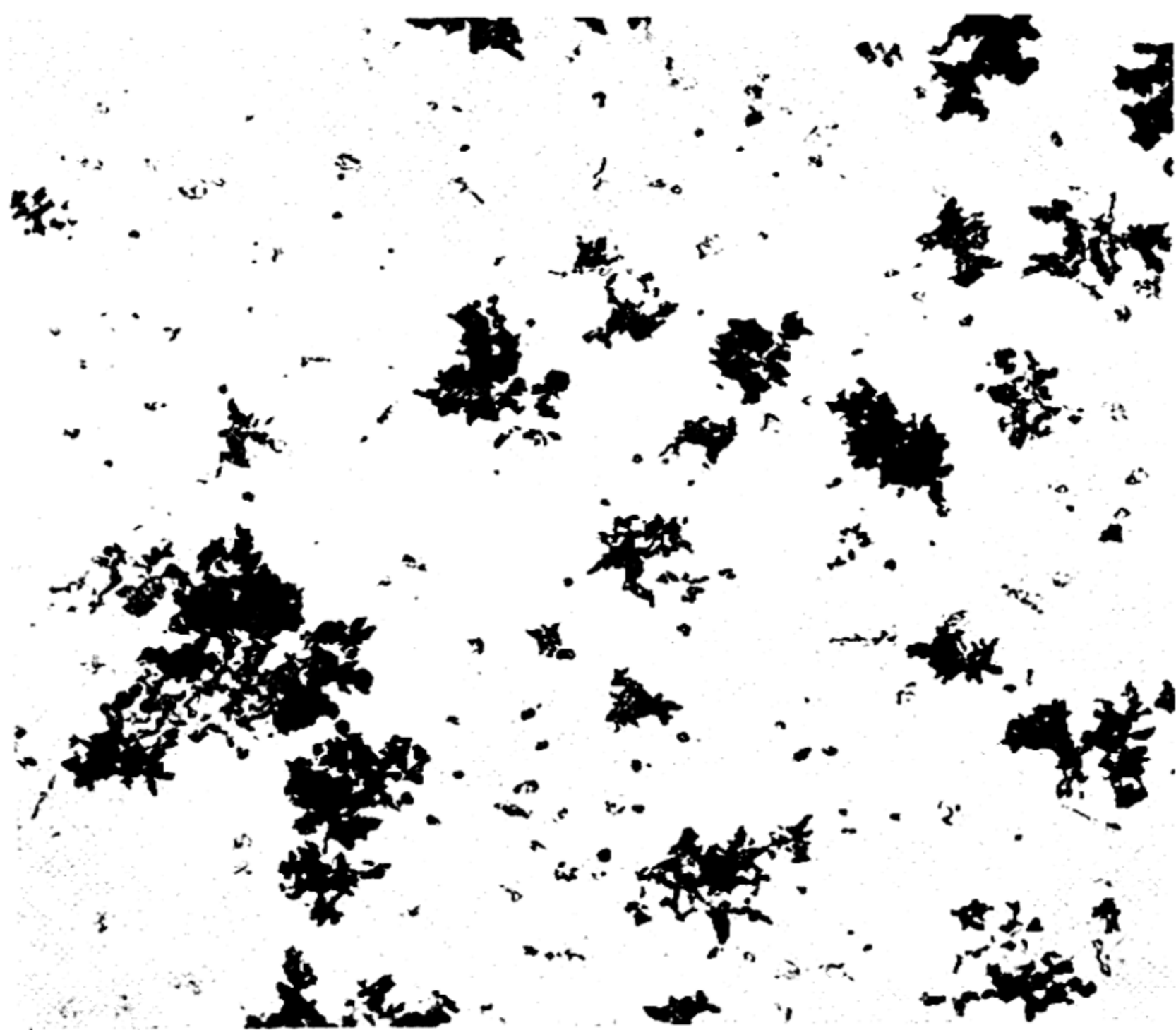


FIG. 20-9. Temper Carbon in Malleable Iron. 100 \times ; Unetched.

The graphite deposited in the solid can be of varied shapes. It may be in a cluster of flakes such as shown in Fig. 20-9, which grow from a solution containing MnS inclusions, or in a much more compact form (Fig. 20-10). Where FeS is present, it becomes a spherulite (Fig. 20-11). In the former cases, obviously the individual flakes grew in rather random directions from a central origin; in the latter case, the flakes, though no longer visible, are arranged tightly and concentrically parallel to the surface. Most of our knowledge in this field is due to the work of Morrogh.

Morrogh's work indicates that the form of graphite depends in large measure upon the type of nucleus upon which the graphite grows.

A nucleus of iron sulphide will produce the dense spherulitic form, and one of MnS will produce the branched, sprawly form.

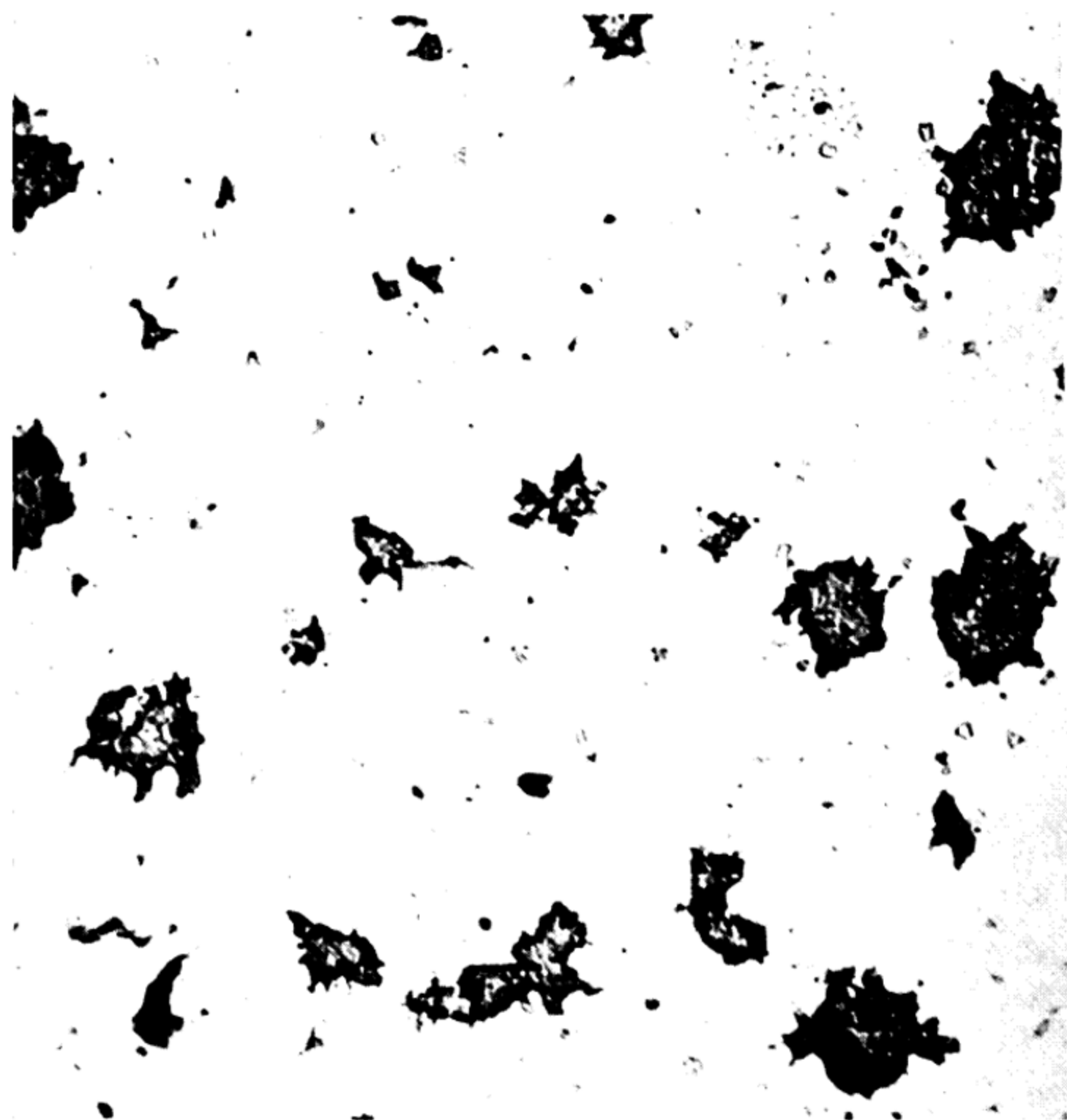


FIG. 20-10. Dense Temper Carbon in Malleable Iron. 100X; Unetched.

It may be that there is a relation to the crystal lattice of the nucleus; FeS is hexagonal, as is graphite, and MnS occurs in both a cubic and hexagonal form.

In the dense spherulite the hexagonal planes of the graphite lattice are at right angles to the radius.

There is here an interesting field of speculation as to the growth of the spherulite, presumably slowly, at right angles to the hexagonal plane, and the growth of the graphite of gray iron and of most blackheart malleable nuclei, apparently rapidly and in the plane of the hexagonal. Does the

crystallography of the inclusion determine the orientation of the first layers of atoms and so of the entire structure?

Reaction Rates during Graphitization of White Cast Iron

The graphitizing process is an interesting example for the study of the kinetics of a reaction taking place in the solid

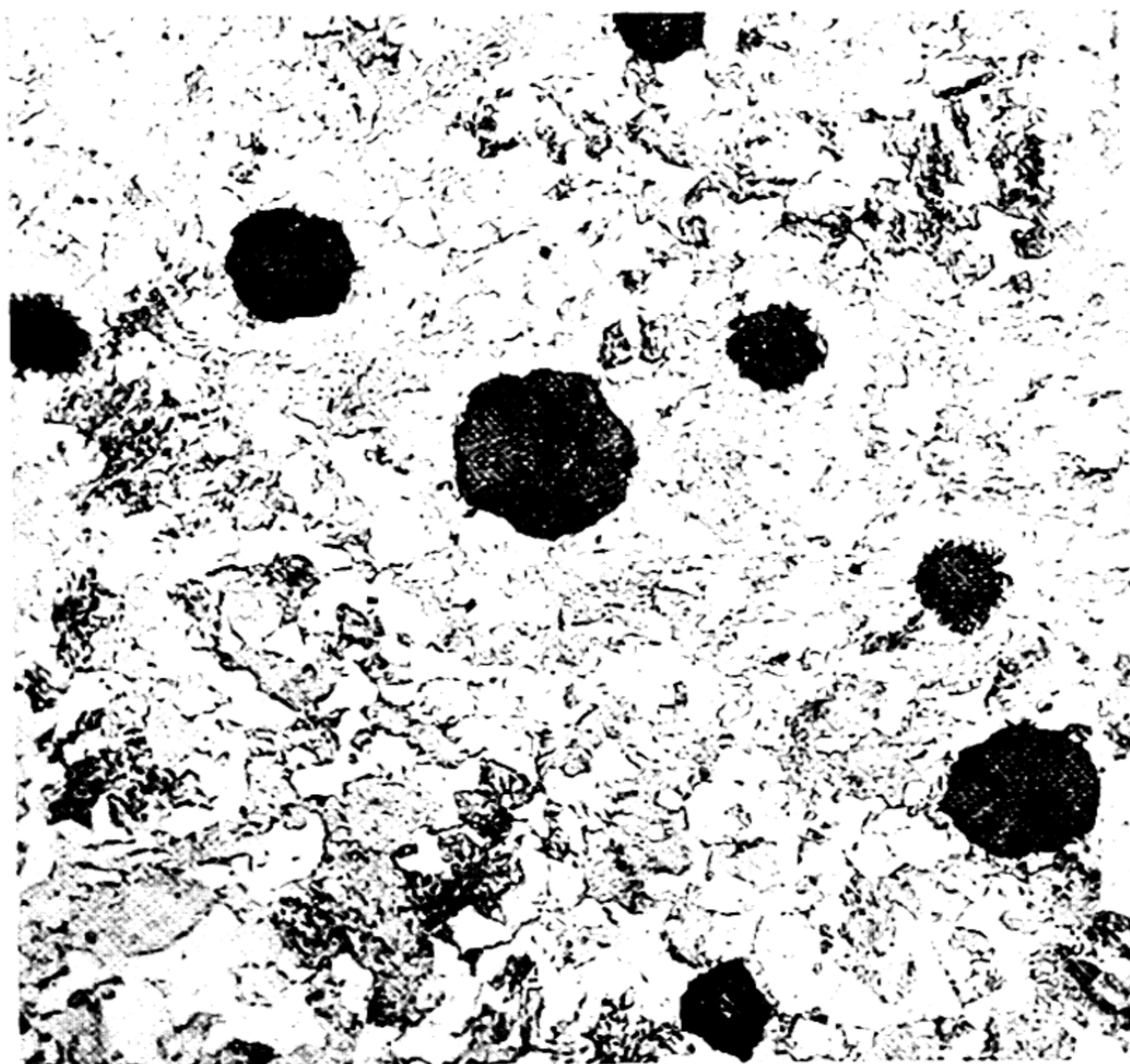


FIG. 20-11. Spherulitic Carbon in White Heart Malleable. 100 \times ; Nital Etch.

state. Reactions in the liquid state proceed too rapidly for controlled experimentation. Below A_1 the metallographic changes proceed in ways that do not lend themselves so far to the necessary simplifying assumptions, but the reactions in gamma iron are pretty clearly understood.

There the graphitizing reaction involves three steps—solution of cementite, migration of carbon to graphite nodules, and growth of graphite—and in addition, at some state, dissociation of cementite. As in all processes pro-

ceeding by stages, the velocity is determined by that of the slowest step. The rates of these several processes have been deduced by the author and are given here in somewhat abbreviated form, covering only the conditions actually realized in malleable metallurgy.

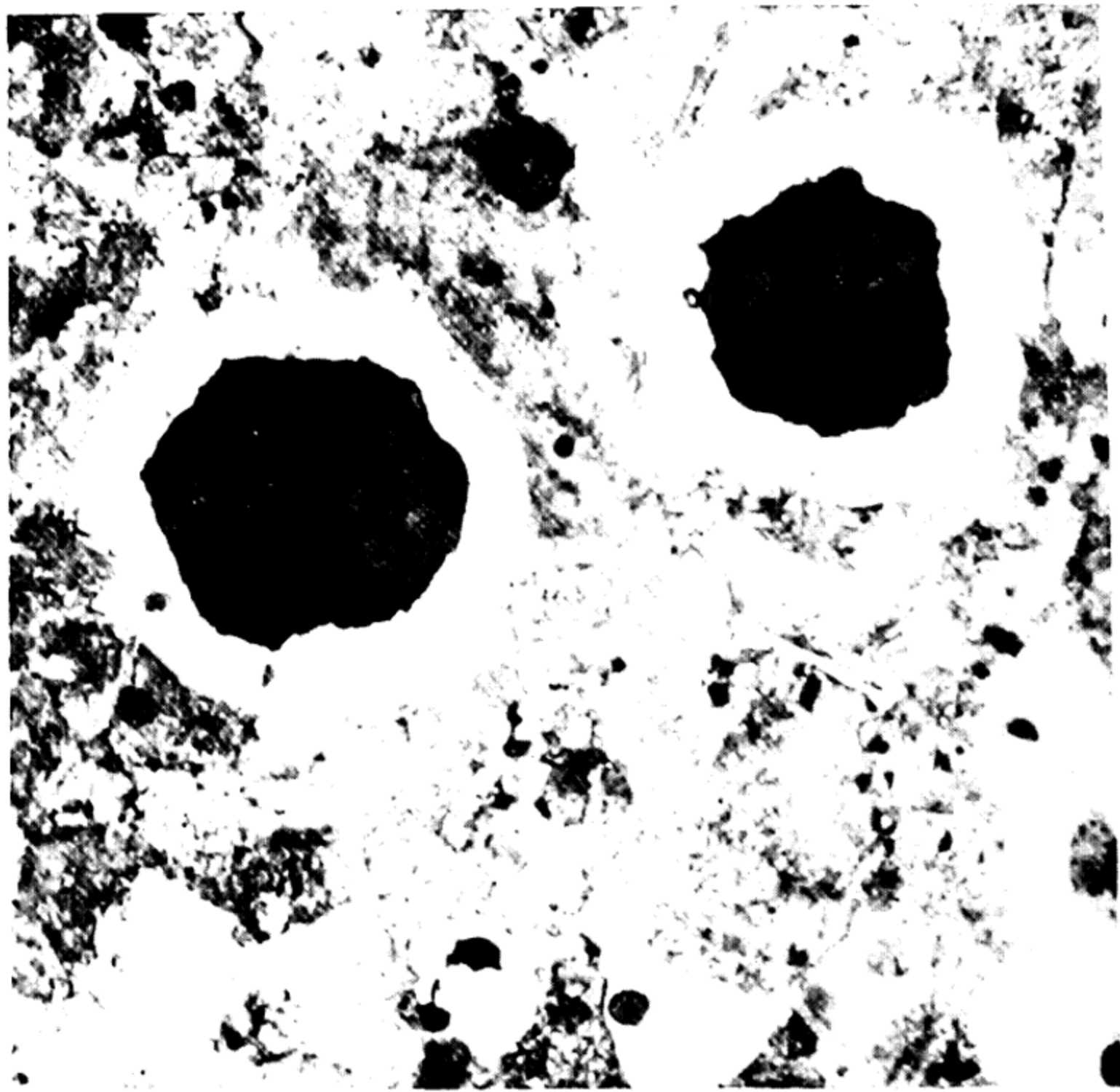


FIG. 20-12. Spherulitic Graphite in Magnesium-Treated Eutectic Gray Iron. 500 \times ; Nital Etch.

Using G to represent the per cent of graphite at time t and C to represent the per cent of carbon originally available for graphitization (the total carbon less the carbon soluble in gamma iron), then if G is less than $0.5236C$ and if the graphitizing rate is conditioned by the rate of solution of cementite,

$$\frac{dG}{dt} = 0.65 N^{1/3} c C^{1/3} G^{2/3}. \quad (2)$$

Here N is the number of graphite nodules per unit volume and c the rate of solution of cementite per unit area of spherical surface of the decementized zone.

If the rate is conditioned by that of graphite precipitation,

$$\frac{dG}{dt} = 14.87 D^{1/3} a G^{2/3} N^{1/3}, \quad (3)$$

where the symbols have their previous meanings and D is the density of packing (that is, the ratio of the volume of graphite in a nodule to the over-all volume of the nodule) and a is the linear crystallization velocity of graphite.

Evidently the two rates are each proportional to $G^{2/3} N^{1/3}$. Which is the slower depends on whether $0.65cC^{1/3}$ is greater or less than $14.87D^{1/3}a$. Note that C is to some extent affected by total carbon, which influences the fraction of spherical surface occupied by cementite.

Within the range of G that is of practical importance, the mechanism of the reaction cannot change. If it is conditioned by solution at one time it cannot be conditioned by migration at another.

If determined by migration, and if G is less than $0.5236C$,

$$\frac{dG}{dt} = \frac{32.58 D^{2/3} K b N^{2/3}}{D^{1/3} - 0.325 C^{1/3} G^{1/3}}. \quad (4)$$

If G is greater than $0.5236C$ and less than $0.972C$,

$$\frac{dG}{dt} = \frac{39.5 C N D^{2/3} b K}{(D^{1/3} - 0.325 C^{1/3}) N^{1/3} C^{2/3}} \left\{ 2 \cos \left[240^\circ + \frac{1}{3} \cos^{-1} \left(1.13 \frac{G}{C} - 0.112 \right) \right] + 1 \right\} \quad (5)$$

If G is greater than $0.972C$,

$$\frac{dG}{dt} = \frac{45.75 D^{2/3} N^{2/3} b K (G - C)^{2/3}}{1.64 C^{1/3} (D^{1/3} - 0.325 C^{1/3})}. \quad (6)$$

The symbols not previously used are b for mass of carbon migrating across unit area in unit time at unit concentration gradient and K for the difference between the A_{cm} and A_{gr} concentration at the temperature chosen.

If the process is determined by dissociation rate,

$$\frac{dG}{dt} = g(C - G), \quad (7)$$

where g is the fraction of carbon as cementite dissociated in unit time.

From these equations it is possible to determine for known constants at what values of C/G the control changes

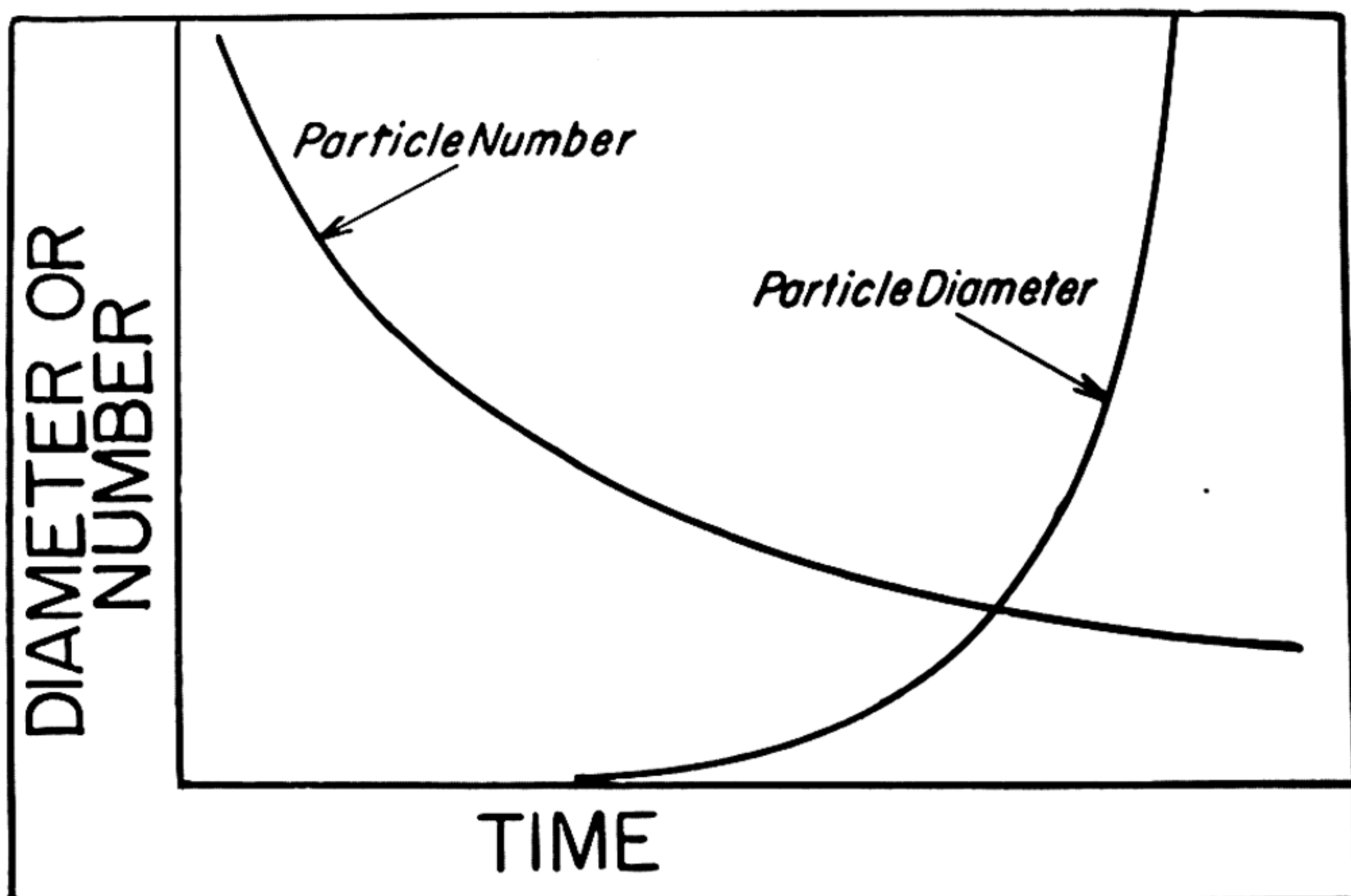


FIG. 20-13. Formation and Agglomeration of Particles on Aging a Copper-Aluminum Alloy. Schematic, after Merica via Sisco.

from one mechanism to the next and by integrating (choosing the correct constants of integration), to compute the entire complex relation of graphite to time.

The process always begins by Equation (2) or (3); one cannot kinetically distinguish between them. After a relatively short time, during which little graphite forms, Equation (4) takes over and the process may continue by Equation (5) or (6), but at the end Equation (7) always takes control.

The result is an S-shaped curve correlating graphite with

time. It begins parallel to the time axis and remains near it for a considerable period; then graphite increases about as the $1\frac{1}{2}$ power of time until it is about half complete, when the curve begins to flatten again and approaches completion infinitely slowly.

Many of the constants are unknown, but these principles will serve to interpret experimental data as to the graphite formed in various times. Also it will be plain that such constants as dissociation rate, migratory rate, and carbon solubility are functions of temperature; hence the relation between the preceding differential equations may change with temperature.

The shape of the time-graphite curve (above A_1) can be used as evidence for the existence of the sulphide films described by Levy. We learned that the beginning of the graphitization curve was an expression of either linear crystallization velocity or rate of cementite solution. The former should not be affected by the presence or absence of films; the latter should.

Many observers have described incubation periods before graphitization begins. Actually these probably are the intervals during which solution rate determines reaction velocity. Since sulphur increases the incubation period, it decreases the solution rate of cementite, by coating its surface, and the results are consistent with Levy's.

The progress of graphitization below A_1 , after completion at higher temperatures, is less well understood, for it depends in a large measure on the metallography established during cooling through the critical zone. If no bull's eyes are formed there, an unusual condition, the logarithm of combined carbon seems to be a linear function of time. Bull's eyes seem to retard subsequent graphitization.

The precipitation of solid phases has been considered above in relation to a system having an allotropic change (alpha-gamma iron). This is by no means essential. For example, copper dissolves in aluminum, which shows no

phase change, or in iron within the alpha range, to a much higher concentration at higher temperatures than at lower.

A given though limited amount of copper can be kept in solution by quenching from an appropriately high temperature and can then be precipitated by subsequent holding at a lower temperature. It is believed that the precipitation phase in such cases is an intermetallic compound of the elements of the system.

Diffusion

The diffusion process by which migration takes place in solid metal is best explained on the following assumption. When a substitutional alloy is heated, some atoms leave the surface layer (attaching themselves elsewhere) and rows of atoms move forward one atom space, leaving a gap somewhere within. If this gap comes opposite a stranger atom, the latter may be able to jump the energy barrier and fill the gap.

The diffusion of substances, in general, obeys the same laws as the diffusion of heat discussed in Chapter 13 but the diffusivity constant equivalent to thermal conductivity may vary with the concentration of the solution.

* The effect of temperature on migrating rate is similar to that on reaction velocity (Chapter 18).

CHAPTER 21

Effect of Alloying Elements on Microstructure of Iron-Carbon Alloys

IN THE PRECEDING CHAPTER, things were made simple and easy of description by considering only the elements iron and carbon. Much remains to be explained that requires consideration of other elements. This leads us naturally to an exposition of equilibrium in ternary (three-component) and more complex alloys.

All cast irons contain more or less silicon, and this silicon is a major item in controlling the formation of graphite. In addition, the steels as well as the cast irons contain at least manganese, sulphur, and phosphorus. The manganese is a contributor to hardenability in steel. Perhaps we can dismiss the sulphur as being present as an inert phase, though this is not too certain near the melting point. Phosphorus in moderate amount in the presence of a reasonably high carbon content does form a third phase that participates in the equilibrium. Alloys in which either or both elements are high will necessitate consideration of the existence of phosphorus-bearing solid phases.



FIG. 21-1. Steadite (Iron-Carbon-Phosphorus Complex) in Cast Iron. 400 \times ; Heat Tinted.

Equilibriums in Three-Phased Systems

The phase rule will point to certain quite essential differences between binary and more complex systems. For example, it tells us that a two-component system, if single phased, has three degrees of freedom, of which one remains after temperature and pressure are arbitrarily chosen. If it has two phases, there are two degrees of freedom, and the system is invariant at an arbitrarily chosen temperature and pressure. For three phases, this system is invariant at a chosen pressure, and for four it is invariant.

This language is perhaps a little high flown; the statements mean that a single-phased, binary alloy can exist over a range of composition or temperature—that is, a given alloy is single phased over a range of temperature and a whole range of compositions at a predetermined temperature. If the system has two phases, however, at a chosen

temperature the two phases have specific compositions. A phase of a given composition is in equilibrium with another at one temperature only, not subject to arbitrary choice, and the second phase must be of a particular composition. Three phases are not in equilibrium except at one particular and specific temperature, and the composition of these phases is not subject to choice. All the foregoing conditions presuppose a selected pressure. There is only one temperature, one pressure, and one set of compositions for which four phases in equilibrium can exist.

Having so reviewed the application of the phase rule to binary systems, let us turn to the three-component system. Obviously, from the phase rule's form, this adds one degree of freedom to those of the binary system for the same number of phases.

Thus, a single-phased field exists over a range of concentrations of each of two components and of temperature. Two-phased equilibrium can exist at a given temperature over a range of concentrations of one component in either phase, but all the other concentrations are then fixed, or if we choose two concentrations from among the three components of each of the two phases, everything else, temperature included, becomes fixed.

Three-phased equilibrium still has two degrees of freedom, so that at fixed pressure one may choose a temperature and perhaps have three phases in equilibrium, with composition not subject to choice.

Four-phased equilibrium (at chosen pressure, remember) is possible only for some one temperature and one set of compositions.

The important difference between binary and ternary systems will be shown more clearly if we consider the eutectoid or eutectic and assume that in both systems we then have three phases (one liquid and two solid at the eutectic point). For binary systems, of two components, the sole degree of freedom is used up in fixing the pressure,

so this equilibrium exists at invariant temperature. In a three-component system, we do not have a eutectic freezing point, but we have a range of temperatures over which three phases of appropriate composition can be in equilibrium. Only if the eutectic breaks up on freezing into three solid phases (or if the liquid consists of two immiscible phases, which is unusual) have we a fixed transformation point.

Representation of Three-Phased Equilibriums

The fact that all the phases participating in equilibrium in any one field do not, in general, have a common concentration in any component prevents adequate representation of many-phased equilibriums on a plane surface, as for example by pseudobinary diagrams in which the third component is held constant. Such diagrams give temperatures at which the phase relationships change but do *not* give the equilibrium compositions of the phases at a given temperature. The only variable common to all three phases is temperature. If it is impracticable to represent the phase diagram by a three-dimensional model, then isothermal sections, not pseudobinary sections, should be used.

Models are difficult to make and carry around and often difficult even to see through, but a ternary equilibrium can be understood on the basis of a series of sections of constant temperature, or so-called isothermal planes. In the writer's opinion, these constitute the only permissible way to represent ternary equilibriums on a flat surface. The isothermal lines represent the contour of the space model just as the surveyor's contours (lines of constant elevation) represent the surface of the ground.

Iron-Carbon-Silicon

The iron-carbon-silicon system has been studied at least as much as any other three-component system, and yet there is much uncertainty concerning the system involving

cementite and substantially no systematic knowledge of the stable system.

In the iron-cementite system, any alloy of over 1.75% C finally freezes at 1130°C, the two solid phases formed con-

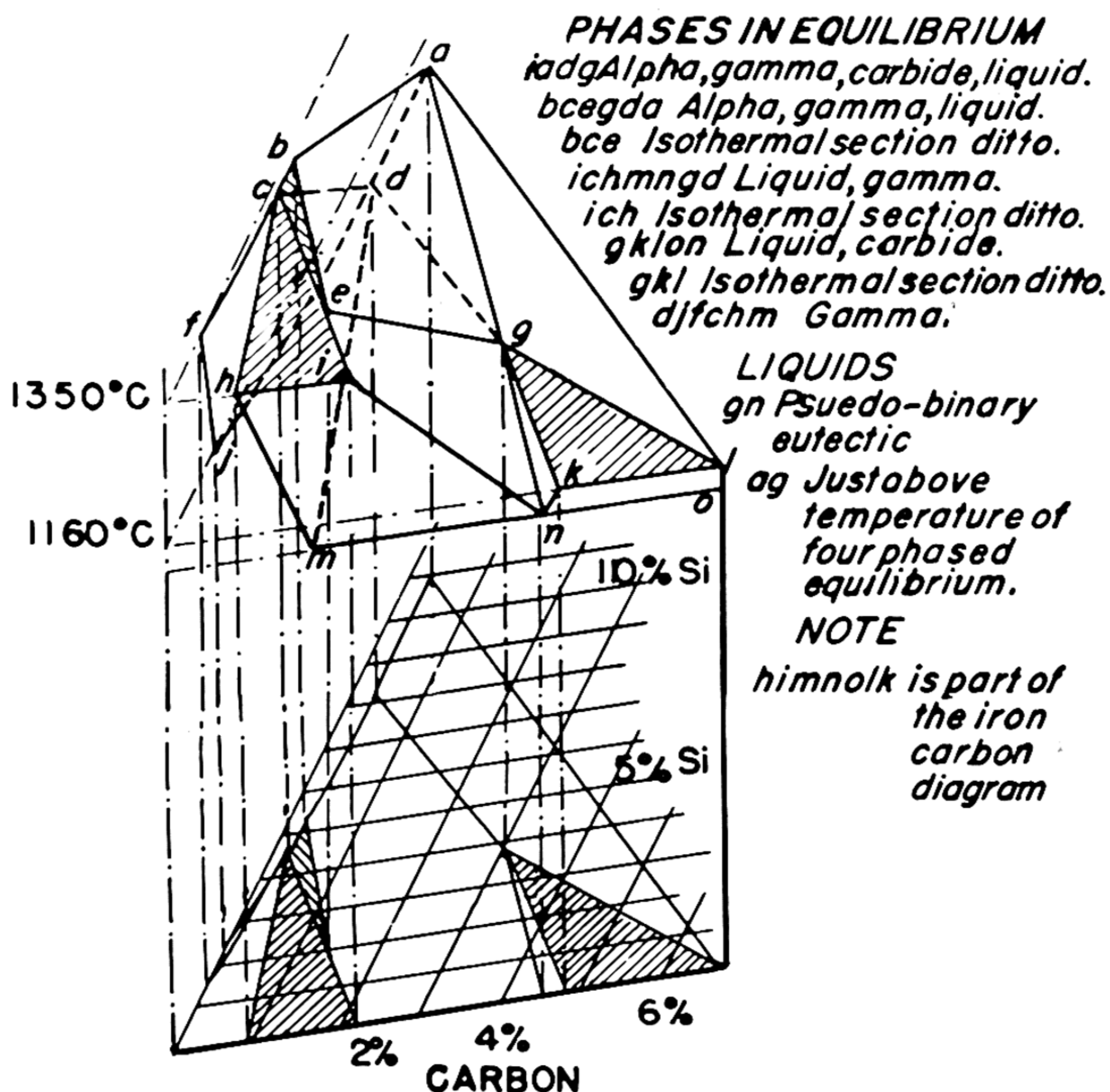


FIG. 21-2. Isometric Projection of Portion of Iron-Carbon-Silicon System. (Based on Greiner-Marsh-Stoughton.)

taining 1.75% C and 6.67% C, respectively, according to currently accepted diagrams. The third phase is a liquid of 4.3% C.

In a three-component, or ternary, system, a four-phased

equilibrium is analogous to a three-phased equilibrium in a binary system in that at atmospheric pressure it can exist only at one temperature, 1160°C in the iron-carbon-silicon system. This temperature, which was a horizontal line extending from 1.75% C to 6.67% C at 1130°C in the iron-carbon alloys, has now become a horizontal four-sided figure at 1160°C , the corners being at approximately 6.67% C and zero silicon, a solution in gamma iron containing about 8.2% Si and 0.35% C, and a solution in alpha iron of similar carbon content but containing about 11% silicon. The fourth, liquid, phase contains about 3.1% C and 3.75% Si. These points mark the composition of the four phases in equilibrium at this temperature. Only alloys falling in this area are capable of four-phased equilibrium, and the area includes few, if any, compositions of foundry interest.

In the three-component system this, however, is not a case of a eutectic freezing, for all alloys having lower silicons and somewhat higher carbons than those of the liquid just described have still lower freezing points. Note also that were there a ternary eutectic, the isothermal eutectic plane would have been triangular, with the composition of the liquid falling within it.

The commercial alloys, lying in the direction of lower carbon and silicon than found in the quadrilateral described, but not too low in carbon, freeze by the deposition from the liquid of either silicocementite or silicoaustenite. They are at least partially liquid down to 1130°C when the liquid contains 4.3% carbon and no silicon. For low enough carbons and silicons, as in steels, they will, of course, be completely frozen before reaching 1160°C .

The freezing of the cast irons, however, proceeds along equilibria between a liquid and a solid phase just like the freezing of the binary alloys, with the exception that the concentration of both silicon and carbon in the two phases requires the use of isothermal sections.

Conjugate Compositions

Assuming, schematically, that the area of the two-phased field at some temperature is the trapezoid (four-sided figure with two sides parallel) shown in Fig. 21-3, this area should be filled by *tie lines* joining conjugate points on the boundary of the liquid and solid phases, which are in fact in equilibrium with one another.

The van Laar equation makes no demands on the number or nature of the solutes; hence the use of straight lines parallel to the edges of the base triangle for the composition of a solid phase should actually be approached moderately well experimentally.

The phase rule says that for two-phased equilibrium in a ternary system there are three degrees of freedom, of which we use up two for fixing a pressure (atmosphere) and a temperature (that of the isothermal plane). If, then, we say that one of the phases shall have a particular concentration of any of the three components (that is, if we select a point on the corresponding boundary of the two-phased field of Fig. 21-3), only one point on the opposite boundary can have a composition in equilibrium therewith. Some theoretical reasoning is possible as to what constitutes conjugate composition, but such reasoning has not sufficient experimental backing to make its conclusions important here.

In the absence of any exact data as to the effect of one solute on the solubility of another, we shall probably not go too far astray in assuming that if the two lines marking the composition of the two phases are divided into the same

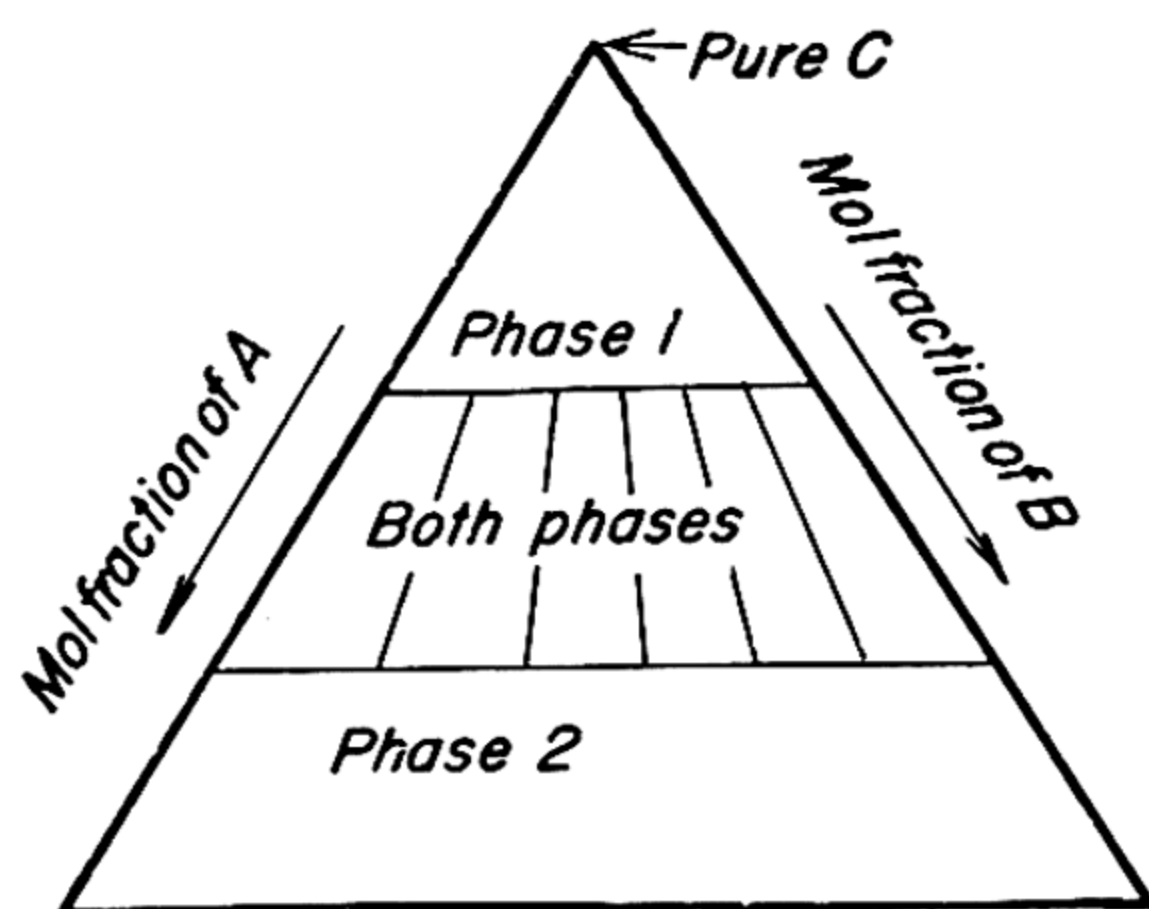


FIG. 21-3. Schematic Representation of Two-Phased Equilibrium Compositions in a Ternary System.

number of equal parts, the points of division will denote conjugate compositions. Tie lines cannot intersect because, if they did, an alloy of the composition marked by the intersection would have two pairs of phases constituting equilibrium, and the phase rule has said that only one pair can exist. Since every point in the two-phased field must lie on a tie line, the sides of such a field must be straight lines.

In Fig. 21-3, a few such lines are drawn for illustration and without pretext at any real accuracy. One such line will pass through the point marking the composition of a given alloy freezing in this manner, and its ends mark the compositions of the solid and liquid phases that are momentarily in equilibrium. About all that is known as to the composition of conjugate points is that for alloys up to, say, 1% silicon and between 2.5% and 3% carbon, the silicon seems to be associated with the cementite; this, if only two-phased equilibrium is involved, should mean that the austenite is silicon free. This is not easily reconciled with any freezing equilibrium. An error in the chemical technique adopted when this matter was studied in the author's laboratory is suspected.

The steels freeze either as gamma iron in equilibrium with liquid or, if low enough in carbon, as delta iron similarly in equilibrium and subsequently converted to gamma iron.

Silicon and Freezing of Gray Iron

Boyle's discussion of the formation of graphite concerned itself largely with events occurring during the freezing of the eutectic, which is a constant-temperature or isothermal process. If we remember that commercial iron-carbon alloys are of compositions that are two phased just before freezing, and hence probably have three-phased equilibrium at the moment of freezing, we observe at once that this equilibrium permits of a variation in temperature.

In a three-component system such as iron-carbide-silicon which we are here considering, an isothermal section will

contain a triangular area within which three-phased equilibrium is possible. The composition of the three phases is that marked by the three corners of the triangle. These three compositions may and probably will change with the temperature. The most acceptable data regarding the system indicate that at the composition corresponding to austenite of maximum carbon content for each silicon content, three-phased stability is at an invariant temperature. For increasing carbon, involving the separation of a carbide, the upper and lower limits of temperature within which three-phased stability can exist both rise, the former more rapidly than the latter. The maximum difference within commercial composition is about 20°C to 25°C .

The composition of the liquid phase in equilibrium with two solid phases changes linearly from zero silicon and 4.3% C at 1130°C to 3% Si and 3.2% C at 1150°C .

As the temperature falls, the liquid becomes impoverished in silicon and enriched in carbon. One or the other of the solid phases must contain the silicon rejected by the liquid.

It is very doubtful whether the system has been studied in enough detail to trace the changes in composition of the solid phases with decreasing temperature. Slow diffusion in the solid state adds to the experimental difficulties.

Certainly no one knows the system iron-silicon-graphite well enough to say anything about it. It seems plausible that the graphite does not contain silicon. It would be possible to have, under the phase rule, some temperature and pressure at which a five-phased equilibrium solid solution in gamma iron-carbide-graphite-solid solution in delta iron-liquid might be possible. Also at a chosen pressure there may be four-phased equilibrium; carbide-graphite-liquid-solid solution may exist at some one temperature. If such a condition exists it is probably in hypereutectic alloys near 1200°C .

The introduction of equilibrium between carbides and graphite is so completely speculative that too much time

should not be wasted in its discussion until more experimental data are available. There is no actual evidence that any conditions exist in which carbides are not converted into graphite below the solidus.

From the view of the gray iron metallurgist, the important practical point is that there is a considerable temperature range in which solid and liquid solutions and carbide can coexist, and where, therefore, conditions are favorable to the progress of the process he practices. This implies an increased time during which graphite can grow and hence increased *primary graphitization*, that is, graphitization during freezing.

Many attempts have been made to generalize as to the relative amount of C and Si that will produce equal tendencies to form graphite on freezing. One of the most recent and apparently best founded is due to Laplanche, who, finding earlier work by Maurer entirely unreliable, came to the conclusion that all irons for which

$$\text{Si} = 1 - \left(\frac{5}{3\text{C} + \text{Si}} \right)$$

has the same value, are likely to produce the same degree of graphite formation at the same cooling rate.

Thus if one knows one combination of C and Si that produces the desired degree of graphitization in a given object (that is, at a given cooling rate), all other combinations acting similarly can be calculated.

The curves are best applied as boundaries between cast irons whose structure is entirely white, mottled, pearlitic, ferritic plus pearlitic, and ferritic. In each case the boundaries apply only to some particular cooling rate.

Manganese atoms are much more like iron atoms than are silicon atoms. Consequently, the system Fe-Mn-C for the ranges of composition in which one is usually interested (excluding the Hadfield steels containing some 12% Mn)

can be fairly well considered merely as iron-carbon alloys so far as the phase diagram is concerned.

The Fe-C-P system freezes with a three-phased ternary eutectic of austenite, cementite, and a phosphide.

Considerable space has already been used to describe one three-component system, the best known, Fe-C-Si. The reader will probably be glad to forego more detailed or more extensive discussion of this and other three-component equilibria.

Multicomponent Systems

The models representing such diagrams are usually constructed, following Gibbs, by representing composition as a point in a base having the form of an equilateral triangle. Need one remind the reader that the sum of the distances from any one point to each of the three sides is the same (the altitude of the triangle)? Temperatures are then measured vertically from this base, and a solid model, in which the boundaries of various phase fields are represented by surfaces, can be built up.

The method cannot be applied to quaternary, or four-phased, fields, for the base would have to be a tetrahedron (three-dimensional figure). To this perpendiculars would have to be erected in a fourth dimension, removing the resulting four-dimensional model from comprehension by our three-dimensional imaginations. Just as we could represent isothermal sections of a three-dimensional model by triangular planes, we could represent such sections of a four-dimensional model by three-dimensional tetrahedrons within which the fields of a constant temperature section of the quaternary model would be bounded by surfaces.

The construction of such a series of models is obviously more difficult and the result harder to visualize than its ternary equivalent. They have been used in slag studies.

For more than four components, the problem becomes entirely incomprehensible, except on the basis of mathe-

matical expressions for the boundaries. Few metallurgists find it profitable to reduce their observations to this form, and hence our knowledge of equilibriums among more than three components is meager at best.

Effect of Alloys on Graphitization in the Solid State

The effect of additional elements on graphitization has been studied most extensively in connection with *secondary graphitization*, that is, graphitization in the solid state, and usually in the gamma iron temperature range.

Elements retarding such graphitization are (in approximate order of potency, beginning with the element of greatest effect per unit weight) H, O, Cr, B (in amounts near 1%), Mn, S, Se, Te, V, Mo, and W. Those favoring graphitization are, in similar order, B (in amounts about 0.002% to 0.5%), Be, Ti, Al, Zr, Si, Ni, Cu, P, and possibly Co, Au, and Bi. No completely satisfactory explanation of their behavior exists. The compound-forming elements S, Se, and Te are suspected to combine with iron to form films in or about the iron carbide, preventing solution and migration; Mn and the rare earths, as well as Ce, will combine with these elements if present in sufficient amount and inhibit this effect. Tin, on the other hand, will combine with the sulphur, even if Mn is present, and the harmful effect will appear, owing to films of tin sulphide.

Vanadium forms a completely stable carbide, but the carbides of Mn, Mo, and W graphitize. White cast irons containing 1% or 2% Mn graphitize above A_1 , although a little more slowly than for lower concentrations, but apparently fail to graphitize below A_1 .

It is a plausible assumption that additional elements might divide between two phases of the iron-carbon system in accordance with the Nernst partition coefficient; that is, the ratio of the (molar) concentrations of the impurity in the two phases would be constant. Silicon and molybdenum are apparently present completely in the carbide phase of

white cast iron. The concentration of chrome is about five times as great in the carbide phase as in the austenite. The distribution of Mn and Ni is somewhat complex.

One must remember, however, that diffusion in the solid state may be very slow and that equilibrium conditions may never be reached. This is well illustrated by the fact that by a suitable technique (combining etching and heat treating in alkaline sodium picrate at a fairly high temperature) the original dendritic white cast iron pattern can be reproduced in malleable iron after the long annealing heat treatment. Of course all the etch shows is a difference of composition. .

The mechanism of graphitization acceleration is practically a sealed book. Elements which, like B and Ti, act in microscopic amounts, may work their wonders by altering the nodule number. Despite much study, we have no systematic explanation of what goes on. Attempts at correlating effects with atom size or configuration have proved unsatisfactory. Elements in the fourth column of the periodic table seem to be likely to be active, and the favoring elements often seem to trend toward the two ends of the table; but all this may be merely "a tale told by an idiot, full of sound and fury, signifying nothing."

Hardenability of Alloy Steels

Another effect of alloying elements on reaction velocities is found in connection with the rate of transformation of gamma to alpha iron. Beginning with the work of Bain and Davenport, experiments have been made by holding steel above its A_3 point until it becomes homogenous and then at some lower temperature, below A_1 , for various times and noting how much time it takes for the transformation to begin and end. Some arbitrary small amount of ferrite is taken as the beginning and some similar small amount of residual austenite (transformed to martensite by quenching) is taken to mark these limits.

For eutectoid steels, a diagram such as Fig. 21-4 results. Such curves are frequently designated as S curves. If the

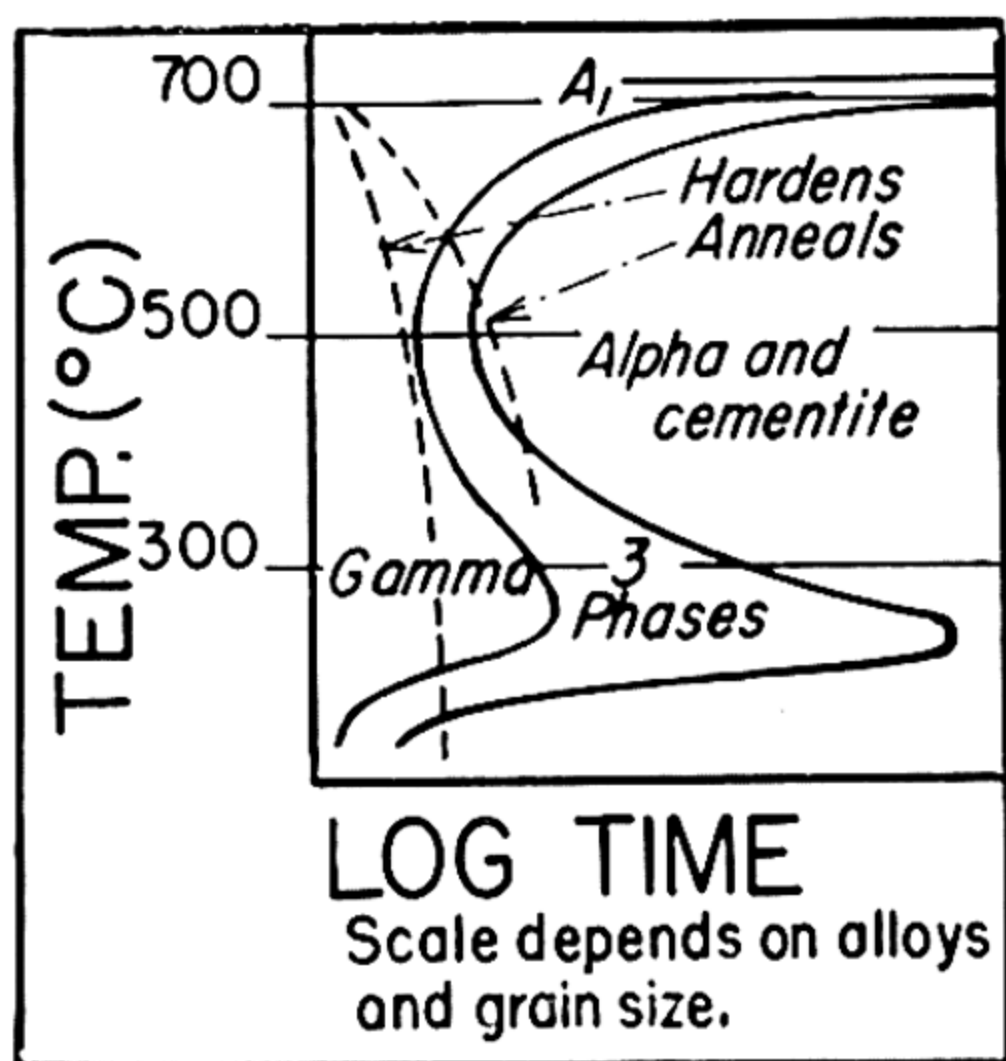


FIG. 21-4. Transformation Times in Eutectoid Steel (Schematic).

steel is hypoeutectoid, the diagram becomes more complicated because of the formation of ferrite between A_3 and A_1 . The curves may take such a form as shown in Fig. 21-5. The addition of any alloy, except perhaps cobalt, to a steel displaces such a set of curves to the right, that is, retards the rate of transformation and hence renders the steel more hardenable. A steel will be martensitic on quenching if the locus of its cooling rate passes to the left of the S curve's nose at about $500^{\circ}\text{C} \pm$, but does intersect the nose at the martensite point, usually near 275°C . If we wish complete conversion to martensite, the time temperature relation should pass to the right of the curve of complete transformation at that temperature.

For very slowly transforming steels, this may be impossible, and residual austenite will remain.

The dotted curves of Fig. 21-4 illustrate schematically cooling rates suitable for complete hardening and complete annealing.

The cooling rate within an article of any size is obviously

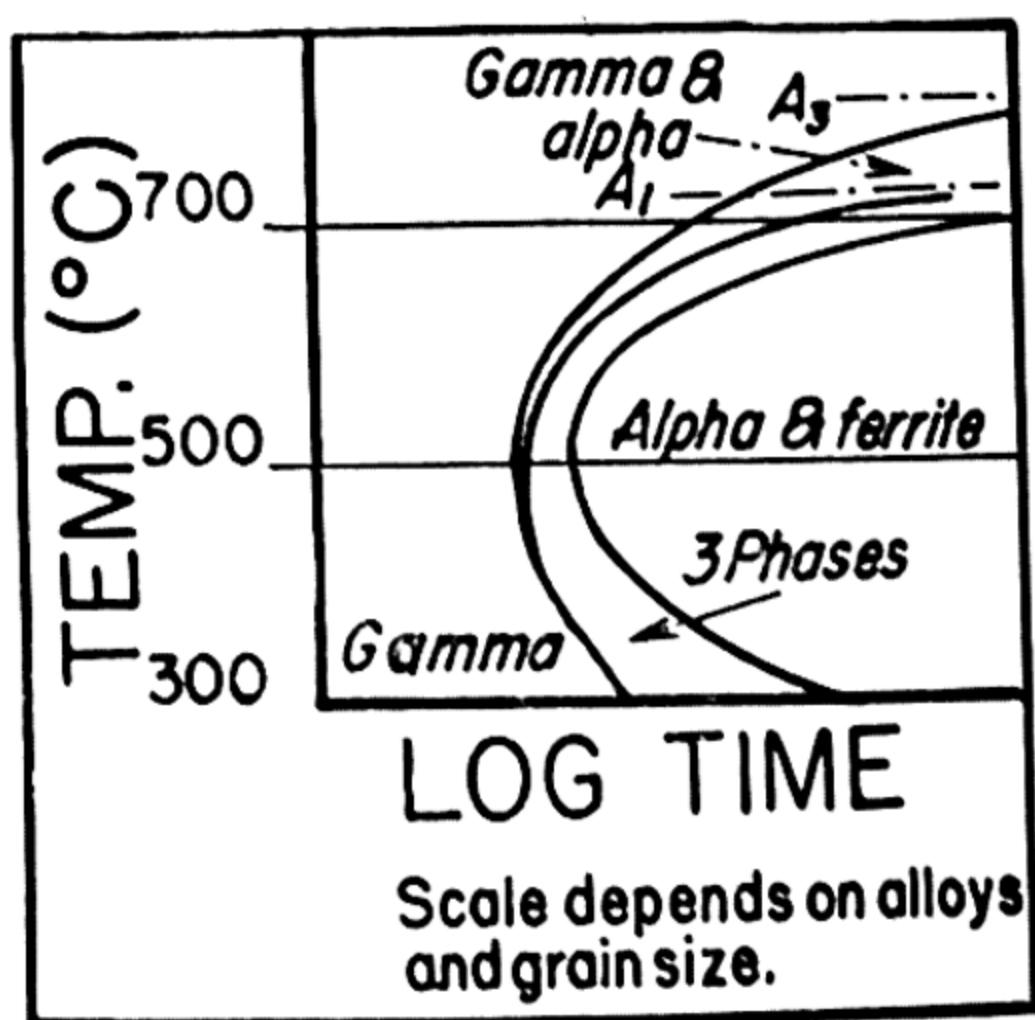


FIG. 21-5. Transformation Times in Hypoeutectoid Steel (Schematic).

different at different distances below the surface and is calculable from the heat-transfer laws.

Hardenability is measured by the Jominy test, which involves measurement of the hardness of a cylindrical specimen at various distances from one end when that end is quenched under specified conditions.

The hardenability of a steel is a measure of the cooling rate required to suppress the transformation during cooling to a given extent. It is expressed as the *ideal critical diameter*, designated as D_i . This is the diameter of a specimen, which if its surface is suddenly cooled to some temperature, from the austenitizing temperature, and kept there, will in the given steel be half martensite and half troostite at the center. Although somewhat cumbersome to define, the use of this type of measurement is convenient in practice. The physicist might have preferred the more elegant but less convenient use of a cooling rate instead of a diameter that compels cooling at a given rate.

The transformation rate is in the first instance a matter of carbon content (and grain size) but is largely modified by the presence of other elements, hence its inclusion here in a discussion of multicomponent alloys.

Grossmann's Relation of Composition and Hardenability

Grossmann's great contribution was a recognition of the quantitative relation between composition and transformation rate as measured by ideal critical diameter. He found the square of the ideal critical diameter (D_i^2) to be proportional to the carbon content, the constant of proportionality being dependent upon grain size. This relationship is such that an increment in grain size by one unit divides the ideal critical diameter by 1.082. Grossmann's conclusions with regard to the contribution of carbon content and grain size to hardenability can be summed up in the expression

$$\log D_i = \bar{1}.7705 - 0.03424Z + \frac{1}{2} \log C. \quad (1)$$

Here D_i is the ideal critical diameter in inches, Ξ (Greek xi) is the ASTM grain size number, and C is the carbon content in per cent.

Now let us consider the effect of alloys on hardenability, the principal purpose of the introduction of hardenability (or transformation rate) in this chapter. Grossmann also found that the effect of most alloys was to multiply D_i by an amount, 1 for no alloy, increasing in direct proportion to the amount of alloy present. Boron and vanadium constituted exceptions, as does silicon above some undetermined value somewhat above 0.40. In his original paper, "Hardenability Calculated from Chemical Composition," in Volume 150 (1942) of the Transactions of the A.I.M.E., Grossmann gave graphs for reading the values equivalent to Equation (1) and the multiplying factors. Since we are here concerned more with principles and general relations, it seems well to translate his empirical observations into their algebraic equivalents.

The result of the study is that D_i becomes the product of a series of factors. The first is D_i from Equation (1) and the others, one for each alloy, each have the form, 1 plus a factor times the elements concentration. Since the logarithm of such a product is the sum of the logarithms of the factors, the entire subject, except for the uncertain elements, can be summed up as:

$$\begin{aligned} \log D_i = & \bar{1}.7705 - 0.03424\Xi + \frac{1}{2} \log C + \\ & \log (1 + 3.333\text{Mn}) + \log (1 + 0.375\text{Ni}) + \\ & \log (1 + 2.37\text{Cr}) + \log (1 + 3.25\text{Mo}) + \\ & \log (1.75 - \log^{-1} [\bar{1}.8751 - 1.1062\text{Si}]). \end{aligned} \quad (2)$$

The weird expression for silicon in the last line represents a fairly good expression for the nonlinear effect of that element. The chemical symbols in Equation (2) represent concentration in per cent. Be it carefully remembered that these mathematical expressions merely reproduce the recorded facts and are not based on any concepts of how an

element retards the transformations. The principles are by no means understood. Also the equations assume that the austenitizing temperature from which the steel is hardened is sufficient to completely dissolve any carbides of chromium; otherwise the hardenability will be less.

An interesting and industrially important point is, then, an expression of the form of these factors for an alloy; with manganese for example,

$$1 + 3.333\text{Mn}$$

implies that a given increment in any element multiplies the hardenability by decreasing amounts as the concentration increases. For example, the addition of $\frac{1}{2}\%$ nickel to a nickel-free steel multiplies the existing hardenability by $1 + 0.375/2$, or 1.1875. The addition of $\frac{1}{2}\%$ nickel to a steel already containing $\frac{1}{2}\%$ nickel and having, because of the absence of some other alloy, the same hardenability as the first, multiplies that hardenability by $1.3750/1.1875$, or less than 1.157. If this is not plain, remember that the addition of the first $\frac{1}{2}\%$ nickel to the second steel multiplied the previous hardness by 1.1875 (to bring it to the hardness of the first steel) and the addition of the second $\frac{1}{2}\%$ nickel, making a total of 1%, multiplied that initial hardness by 1.3750, all from line 2 of Equation (2).

As a matter of hardenability, therefore, elements are more efficient when used in complex multialloy steels than in carbon steels with but one alloying element. The cost of securing a given hardenability is another matter.

Materials of Molds

IN THE PRECEDING CHAPTER we may have learned what would happen, metallographically, during the freezing of alloys. The foundryman's principal purpose is to have metal freeze as a casting of a desired form. Consequently he pours his liquid metal into a mold of appropriate shape.

This means that we must make a mold of something that can be filled accurately with liquid metal and that will resist the effects of heat and abrasion incident to this process.

Metal Molds

Die castings and some other permanent mold castings are poured into metal molds that are provided with vent holes through which the air in the mold can escape as displaced by liquid metal. It is by no means necessary that the metal mold shall have a higher melting point than that of the metal being cast. Steel castings can readily be cast in copper molds.

It can be shown that if two great slabs having temperatures θ_1 and θ_2 , conductivities κ_1 and κ_2 , and diffusivities h_1^2 and h_2^2 , respectively, have their faces brought into

contact, the resulting initial temperature at the surface θ_0 will be

$$\theta_0 = \frac{(\kappa_1 \theta_1 / h_1) + (\kappa_2 \theta_2 / h_2)}{(\kappa_1 / h_1) + (\kappa_2 / h_2)}. \quad (1)$$

Remember that diffusivity $h^2 = \kappa / \rho c$, where κ is conductivity, ρ is density, and c is specific heat. This equation will show that in such a case the mold face does not reach the melting point of copper.

Equation (1) involves the assumption that the temperature of the surface of contact does not change with time. This is justified by the stated conditions of very large masses and infinitesimally small time. It is quite obvious that this condition does not necessarily exist indefinitely, for if the specific heats of the two masses were c_1 and c_2 , respectively, and the masses were equal, plainly at equilibrium (temperature throughout θ') we should have

$$\theta c_1' + \theta c_2' = \theta_1 c_1 + \theta_2 c_2,$$

or

$$\theta' = \frac{\theta_1 c_1 + \theta_2 c_2}{c_1 + c_2}, \quad (2)$$

whereas Equation (1) could be rewritten

$$\theta_0 = \frac{\sqrt{\kappa_1 \rho_1 c_1} \theta_1 + \sqrt{\kappa_2 \rho_2 c_2} \theta_2}{\sqrt{\kappa_1 \rho_1 c_1} + \sqrt{\kappa_2 \rho_2 c_2}}. \quad (3)$$

The two are not necessarily or even usually identical. The conformity would be still worse if the slabs were not infinite or if they were of finite thickness, uninsulated on the faces.

The texts on the Schmidt method give constructions that are apparently not limited by such conditions but that assume at each step the constancy of temperature of the interface. Since the solutions may themselves lead to a change of temperature at that surface, the construction is inconsistent within itself, though it may lead to useful approximations. In view of the method's limitations, it

may well be omitted here. The reader who requires the information will find it described in Research Bulletin No. 98 of the Purdue University Engineering Experiment Station.

Commercial castings are almost always produced in sand molds, either green, that is, damp, or dry.

Sand Molds

Molding sands for the production of green sand molds consist almost invariably of rounded quartz grains that have been naturally or synthetically coated with a thin layer of plastic clay. Occasionally cereal or starch binders are added to strengthen sand, and rather frequently sea coal, which is coal dust crushed to about 200 mesh size, is added to produce a smoother surface.

Dry sand molds are often produced of similar sands, usually with cereal binders, and then baked. Cores and some molds are made of quartz sand mixed with drying oils, rosin, starches, sugars, and other organic binders that, on baking, will hold the sand firmly together.

Consider the basic quartz grains. Quartz is used as being refractory and cheap. Other refractories, such as zirconia and carborundum, have been suggested, despite their cost, where greater heat diffusivity is wanted to accelerate freezing. Some disappointment may be expected. A granular material conducts in two ways, by direct conduction within grains and by radiation from grain to grain. At low temperature the former is more important; at high temperatures, the latter.

Heat transfer by radiation is in no way related to thermal conductivity but depends on the emissivity of the surface, which in the space between grains may trend toward unity for all materials. Since the heat transferred by radiation is perhaps two-thirds of the total, evidently conductivity is not a very complete measure of a material's quality for such purposes.

Owing to the contribution made by radiation, the conductivity of a sand decreases as the grain size decreases, because the temperature difference between adjacent sand layers is less for a given temperature gradient in the sand as a whole, and, as already explained, under radiation the heat transfer is proportional to the fourth power of the temperature of the two bodies between which radiation occurs.

Let their successive layers of sand have the temperatures $T + 1$, T , and $T - 1$, then the heat transfer per unit area between the first and second layers, per unit area, is

$$\alpha[(T + 1)^4 - T^4] = \alpha(4T^3 + 6T^2 + 4T + 1).$$

If the central layer were omitted it would be

$$\alpha[(T + 1)^4 - (T - 1)^4] = \alpha 8(T^3 + T).$$

The second expression is greater than the first if θ is large compared to 1 (that is, if the temperature is large compared to the temperature difference between layers).

Convection does not play much of a part in heat transfer through a dry granular material, but sands containing moisture or organic material evolve gases at the temperature of casting; these hot gases are driven out through the spaces between sand grains, imparting heat to them and so adding to the apparent diffusivity of the sand by a mechanism again entirely unrelated to the conductivity of the sand mineral. The problem of the contribution of the flow of steam in a damp sand to the cooling rate of castings has only recently been successfully approached by Paschkis for the American Foundrymen's Society, no data having so far been published.

The need for porosity in a molding sand arises altogether from the need for disposing of these gases, liberated in the sand body, and not at all from the need of permitting air to escape as the metal enters. The latter could be readily provided for by openings (pop-offs) through the mold.

Rounded sands are more porous or open than angular ones because, as can be shown, a closely packed mass of spheres contains more voids than an assemblage of any other form of solid. Such a close-packed mass of spheres contains just under 48% of spaces, regardless of the size of the spheres. This does not mean that gases will flow equally readily through such assemblages, regardless of grain size. The ratio of surface of spheres to volume of voids increases as the grains are of decreasing size, and the number of times the air current has to change direction is in inverse proportion to grain size, so that small-grained sands impede gas flow more than large grained. The point is that size for size, spherical grains of uniform size permit easiest flow.

Permeability and Grain Size

The mathematics covering the flow of gases through granular media has been the subject of study. Because sand is usually an assemblage of grains differing widely in size, such studies are of little use in connection with molding sands. Also, we have seen that the amount of gas that has to flow through the sand depends on the moisture and binder content of the sand and therefore is only incidentally related to its grain size. Furthermore, the outflowing gas is at high temperature near the casting and is near room temperature further away from the casting, so that the volume flowing past a given cross section during a given time varies. All this makes the analytical study still more complicated. A reasonably useful generalization is that the rate of flow through any such mass is proportional to the square root of the pressure.

Fortunately quite simple means exist for measuring the *permeability* of sand directly by measuring the time required for a given volume of air to flow through a given sand body, or the volume flowing in a given time, in either case under a known pressure. This adequately measures the quality

of a given sand, which generally satisfies the foundryman. There is seldom any need for computing flow rate through a given mold.

It would be useful to be able to predict what additions, in terms of amount and grain size, are required to alter the permeability of an existing sand. The problem is obviously extremely complicated.

In dry sands of a single grain size, with constant ramming, the air flowing in unit time, at a given head through a column of given size, is approximately directly proportional to the diameter of the grain. Mixtures, however, behave in a much more complicated fashion, as shown in Fig. 22-1.

When coarse grains are added to fine, the permeability first decreases and then increases to the permeability of the coarse size. The development of a minimum is most marked, the finer the original sand and the coarser the addition. When mixtures of 60 mesh and 40 mesh are reached, the development of a minimum disappears.

The minimum permeability is generally found in the general region of 30% coarse sand. When the two grain sizes are nearly equal, a maximum of permeability may occasionally be encountered.

When sands are wet, the permeability always increases and finally reaches a maximum at around 5% moisture. This is maintained over a considerable range of moisture, say up to 10% or more, and then the permeability drops sharply. The increase in permeability is most marked, the finer the sand. For sands coarser than 40 mesh it becomes negligible.

All these phenomena might, with detailed study, perhaps be explained by whether smaller grains plug the openings between larger or merely wedge the latter apart, by whether a large grain can be substituted for many small ones without much interference with the latter's packing, by the swelling of clay when moistened, or by the cohesion or sticking together of several small moist grains.

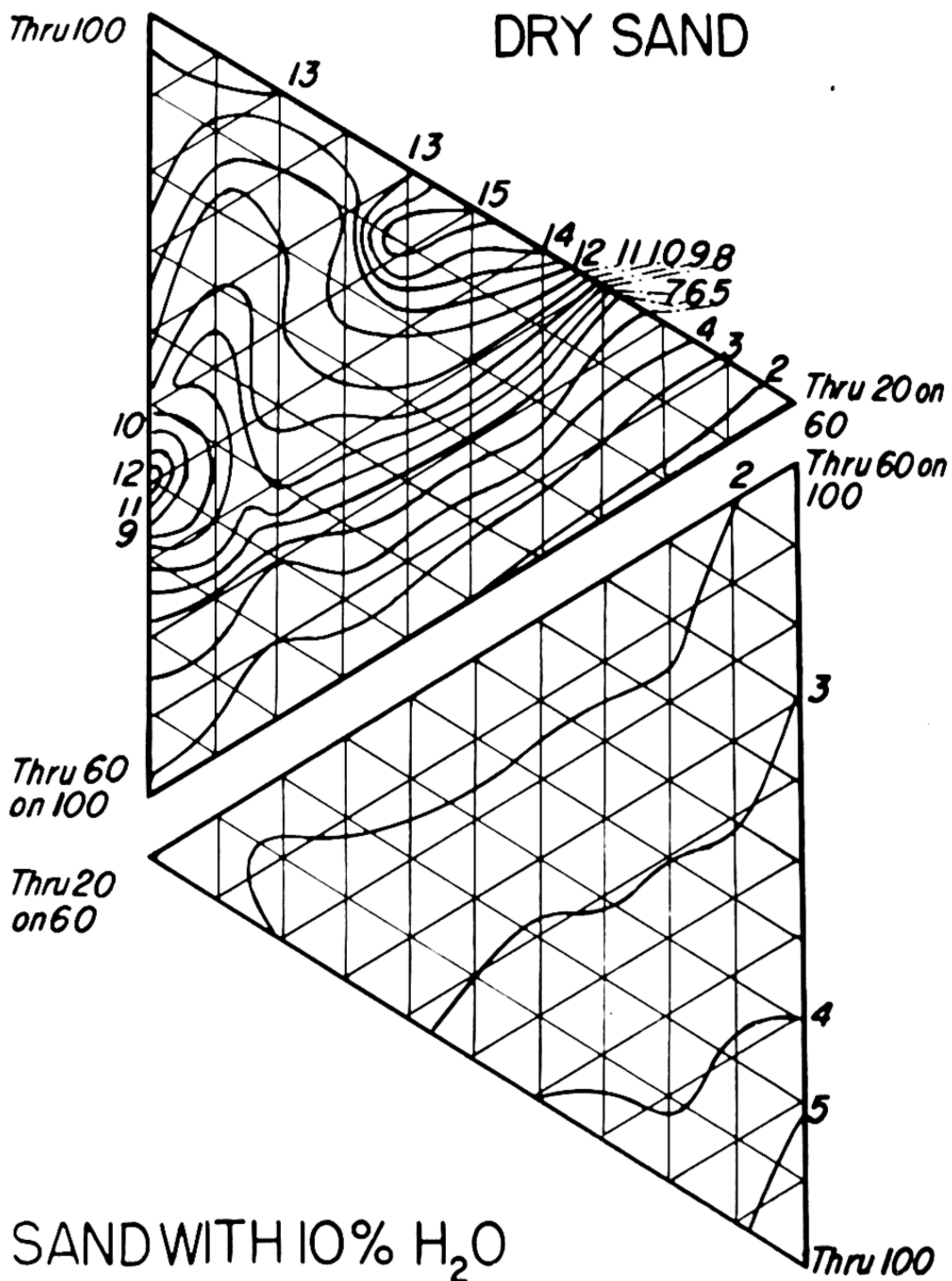


FIG. 22-1. Flow Time through Sands of Various Grain Size Distribution. Numbers at Contour Lines Are the Time in Minutes for a Given Volume of Air to Flow through a Sand Mass of a Particular Form at a Particular Pressure. They Must Not Be Confused with AFA Permeability.

The permeability of mixtures of three or more sizes becomes exceedingly complicated and incapable of generalization. Direct measurement presents about the only approach.

The relation that the rate of air flow under constant head is proportional to the diameter of the grain has some logical explanation. Consider a cube in the sand mass having the center of a grain at each corner, the grains, assumed spherical, touching one another. The volume of the open space in this cube is

$$8r^3 - \frac{4}{3}\pi r^3 = 3.81r^3.$$

The surface of this void is the surface of one sphere, equal to $4\pi r^2$. The average cross section of the void is

$$\frac{3.81r^3}{2r} = (1.9+)r^2,$$

and the average perimeter of the void is

$$\frac{4\pi r^2}{2r} = 6.28r.$$

The ratio of perimeter to area is thus

$$\frac{1.9r^2}{6.28r} = (0.3+)r.$$

The numerical coefficient is not important in the reasoning, but we see that the ratio of perimeter to area is proportional to r . We shall see in the next chapter that this ratio is often a measure of the resistance to flow, and apparently under the conditions of the present experiment this was approximately true.

Clay Bond

Green sand molds are held together by films of clay surrounding the individual grains and coalescing at the points where adjacent grains touch. Our systematic knowledge of the bonding action of clays is mostly due to

Grim, upon whose ideas the following discussion leans heavily. For more detailed treatment Bulletins 357 and 362 of the University of Illinois may be consulted.

The bonding clays, as found in nature, are impure representatives of four types of mineral species. The earliest, in point of use, was kaolinite, sometimes called China clay, which is a constituent of fire clays. Chemically it is $(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10}$, a hydrated silicate of aluminum.

The next to come into commercial use, and now perhaps the most popular, is montmorillonite or bentonite. Chemically it is $(\text{OH})_4\text{Al}_4\text{Si}_8\text{O}_{20} \cdot n\text{H}_2\text{O}$. The western bentonites have the Al partially replaced by Mg, the southern bentonites have Fe and perhaps some Mg replacing a part of the Al. If the replacement is largely by Fe and a considerable amount of Al has been replaced, the mineral has a different name, nontronite. The montmorillonites containing Mg and little Fe adsorb onto their surfaces considerable amounts of sodium ions, while those containing Fe adsorb calcium and sometimes hydrogen ions. These adsorbed ions have significance with regard to binding power and refractories.

The mineral halloysite has been long known, but its use as a binding clay was but recently suggested by Grim. There are two kinds of halloysite, differing in the ratio of hydroxyl groups to oxygen atoms, $(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10}$ and $(\text{OH})_{16}\text{Al}_4\text{Si}_4\text{O}_6$. The latter type loses water easily at very moderate temperatures and becomes converted to the former. Note that the lower hydrated halloysite has the same composition as kaolinite, although their crystal lattices are different. The metallurgist would think of them as two allotropic forms of the same substance.

The fourth mineral, also not yet well known in foundries, is illinite, whose composition is rather variable and is written by Grim as $(\text{OH})_4\text{K}_y(\text{Al}_4\cdot\text{Fe}_4\cdot\text{Mg}_4\cdot\text{Mg}_6)(\text{Si}_{8-y}\cdot\text{Al}_y)\text{O}_{20}$. Though unusual with regard to the occurrence of Mg twice, the formula follows Grim correctly.

Since the clay minerals are to coat the quartz grains uniformly, it is desirable that their ultimate particle size be small. Also the presence of foreign matter, especially if in larger particles, is a disadvantage. Montmorillonite consists of minute flakes, 1 molecule thick if we can use that term. They swell and disintegrate readily in water. Halloysite is composed of rod or lath-shaped units, quite long in one direction as compared to the other two. Illinite and kaolinite do not readily break up into small units when milled but remain as mixtures of approximately equiaxed crystals and flakes. Accordingly, (especially kaolinite) they form irregular coatings.

The mechanism of clay bonding can best be described in terms of montmorillonite, which is experimentally best suited to the investigation. Each flake of this mineral consists of a series of layers of atoms arranged according to well-defined patterns. The outer surfaces contain only oxygen atoms, constituting the corners of the bases of tetrahedrons. A little further in, there is a layer of silicon atoms at the centers of gravity of these tetrahedrons. Still further in, at the level of the vertices of the tetrahedrons, there is a layer of oxygen atoms and of the atoms comprising hydroxyl, and in the center a layer of aluminum atoms. This sequence is repeated for each flake of the parent mineral.

The layer of clay on the surface of a quartz grain, though extremely thin, contains very many such units. Before the mechanism of clay bonding is fully developed, some 1600 flakes make up the thickness of the layer, and a maximum of green bond compression increases until the layer is four or five thousand flakes thick. In terms of the AFA standard molding sand this means that 5% western bentonite is needed to establish the mechanism and some 12% to 15% to give maximum strength.

Water can penetrate the layer of clay minerals and will be adsorbed on the (oxygen-containing) surfaces of the

flakes. This is not mere wetting; the water becomes part of the crystal lattice and has the rigidity characteristic of crystalline substances. If the water layer is three molecules thick for western bentonite (four for southern), the maximum strength of the clay coating is developed, and the sand has maximum green strength. If more water is added, some is present as an excess of ordinary liquid water, and the sand becomes weaker. The addition of water has constantly and considerably increased the bulk of the sand and decreased its bulk density, after a given ramming. For the western bentonite the minimum bulk density is reached when the water layers between the flakes of clay mineral are four molecules thick. Presumably additional water is merely held in the interstices between grains, adding mass but not volume to the total bulk.

It is said that molding sands work best a little wetter than the point of minimum bulk density. Their permeability is best at that point of course.

Since this is not a monograph on molding sands, space can hardly be given to an analysis of the differences in behavior of the several clay minerals. The principles are alike, though the numerical details would differ.

The facts may be sufficiently summed up by saying that with very minor exceptions the maximum green compression strength attainable with any given amount of clay runs in the following descending order: southern bentonite, western bentonite, halloysite, kaolinite, and illinite. The maximum green strength with optimum clay coating runs similarly: southern bentonite, western bentonite, halloysite, illinite, and kaolinite.

Water penetrates but slowly into halloysite or illinite coatings on sand. Hence if there is liquid water in these coatings when the sand is rammed, then, on standing, this water may penetrate elsewhere in the clay and form the films of hard water upon which strength depends. Such

sands air-set, that is, become stronger on standing, even without loss of water.

If molds are dried, the clay films, and particularly the accumulation of clay where quartz grains touch, harden, and the dried mold increases in compression strength. Up to a certain point, an increase in moisture increases dry compression strength, a result attributed to the lubricating effect of liquid water forming the foundation of dense and homogeneous masses of clay substance.

The refractoriness of silica-molding sand is determined largely by the refractoriness of the clay. Bentonite is relatively unrefractory. Also if free basic oxides are present reaction with the silica may produce fusible compounds.

Organic Binders

The binders used to hold cores together fall into a number of classes, as follows:

(1) Drying oils, notably linseed and tung (China wood) which, on heating moderately, dry by adsorbing oxygen and becoming converted to leathery films.

(2) Rosin, which at the temperature of the core oven melts to a liquid that collects mainly at the points of contact of sand grains, solidifies on cooling, and sticks them together.

(3) Various solutions of sugars that lose water on drying, become stickier and stickier, and finally on cooling stick grains together somewhat like rosin.

It is important to note that while rosin sets only by virtue of temperature, as do also the thermosetting plastics, oil cores require access of oxygen in order to bake, and the syrups require the removal of water vapor from the oven atmosphere.

Roughly speaking, the amount of binder required for a given strength depends on the amount of sand surface to be coated. Coatings of similar thicknesses on grains of

different sizes give similar results. Since many binders are viscous, they must be diluted by kerosene or naphtha to permit them to spread, and also they spread better on damp sand grains than on dry.

In view of the enormous surface presented by clay particles, these, if present, will hold enormous amounts of oil binders without contributing much to the core strength.

Molds, especially of coarse sand, are often treated with facings of graphite or silica flour, the former dusted on and smoothed with a trowel, the latter often sprayed on, suspended in a drier. The purpose is to produce a surface whose openings are too small to admit the molten metal.

Sea coal, though a fine powder, functions by a different mechanism. When heated by incoming metal it distills hydrocarbons (ethylene and the like), which maintain sufficient gas pressure in the sand pores to keep out the iron. An excess of sea coal greatly weakens the sand, and the evolution of gas may in such cases produce rifts in the sand surface and do more harm than good.

Fluid Mechanics of Casting

HAVING MADE A MOLD, we now come to the most important characteristic aspect of the foundryman's art—also that which has so far received the least systematic study. This is the process of filling a mold with liquid metal and causing it to solidify without internal voids. In the language of the shop this is *gating and feeding*.

The problem has two entirely distinct but related aspects. The first, to be considered in this chapter, relates to the properties of liquid metals that determine the conditions to be met, and to the laws of flow of liquids commonly studied as hydraulics. The second relates to the design of runners, gates, feeders, and other equipment calculated to produce the most desirable conditions for the purpose. This we shall consider in the chapter immediately following.

The liquid state is not so clearly understood as the crystalline state, in which atoms occupy certain regular positions in a pattern, characteristic of a given substance, or the gaseous state, in which the molecules move about in complete disorder. There are interatomic forces in liquids. We know that liquids hold together and do not disperse in all directions as gases do. They have a given characteristic

density at a given temperature and pressure; hence they have a specific mean interatomic distance. We learned about van der Waals' forces in Chapter 3.

In discussing equilibrium during freezing in Chapter 7 we had to deal with molecules (whether monatomic or not). The organic chemist finds it useful to accept the existence of molecules in liquid solutions. The chemist recognizes dissociation of molecules in solution. In Chapter 19 was mentioned the moot question of whether cementite molecules can exist in liquid iron.

Viscosity of Liquids

There appears to be some acceptance among the X-ray fraternity that a substance in the liquid state still has some regularity of structure. Small groups of atoms exist having somewhat the atomic arrangement existing in the crystalline form, but this regularity does not extend over any considerable volume. With a few exceptions, substances are less dense at their freezing points in the liquid than in the solid state, so that there are voids or holes between atoms of liquid which other atoms might occupy.

A given atom of liquid thus finds itself near other positions where it would have the same free energy but is separated from them by an energy barrier. It would temporarily have to have a greater energy in order to pass through such a region. Temporarily the kinetic energy of the atom, due to temperature, may enable it to move from place to place over these barriers.

Under gravitational or other forces there may be near-by positions, corresponding to an even lower energy state, to which the atom will want to move if it acquires sufficient energy to leap the hurdle. The aggregate of such atomic movement constitutes flow, and it is at once evident that rate of flow under a given force depends on the number of atoms that jump in a given time. This number, in turn, depends on the chance that an atom will become possessed

of enough energy to jump, and this again depends on the mean kinetic energy, that is, on temperature.

The resistance to flow of a liquid is viscosity. It is measured by the force required to move a surface in the liquid, of unit area and situated at a unit distance from a parallel stationary surface, at unit velocity in a direction parallel to itself.

In the cgs system force is measured in dynes, and the corresponding unit of viscosity is the poise, named after the first syllable of the name Poiseuille, a pioneer investigator in this field. Need the reader be reminded that the force of gravity acting on a gram of mass is 980.665 dynes, the number being the acceleration due to gravity in cgs units?

From the discussion of the origin of viscosity it is evident that it decreases rapidly with temperature.

A relation having experimental backing for many liquids is

$$\eta_T = Ae^{b/T}. \quad (1)$$

Here the viscosity at T° Kelvin is η_T , and A and b are experimental constants specific to a given substance. The Greek eta (η) is the symbol of viscosity.

Owing to the experimental difficulties, the viscosities of liquid metals are not too well known in many cases. There is a direct relation between the coefficient of thermal expansion of a liquid and the change of viscosity with temperature.

A useful approximation for foundrymen is that the viscosity at a derived temperature, calculated by dividing the existing Kelvin temperature by the liquidus temperature of the substance, also on the absolute scale, often does not differ very greatly for different metals. A few values are plotted in Fig. 23-1.

Surface Tension

Viscosity is concerned with how fast a liquid will flow under a given force. Surface tension is concerned with

the size of orifice a liquid can enter. We have already encountered this property in Chapter 8.

If we have a particle of substance in contact with another substance, ordinarily the atom very near its surface will be attracted either more or less strongly by atoms of like kind within the body than by atoms of another kind, or of a different degree of dispersion, in the environment.

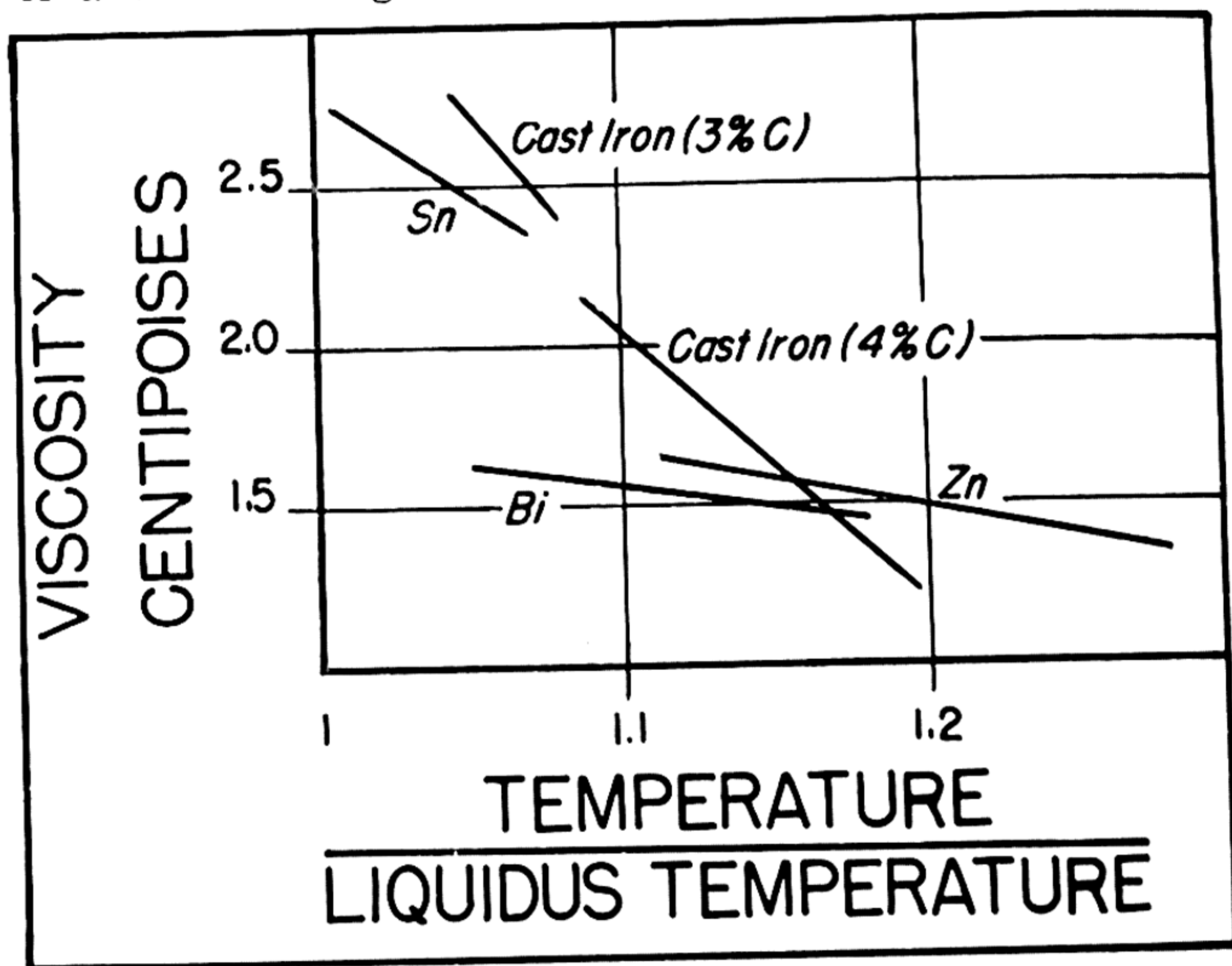


FIG. 23-1. Viscosity-Temperature Relations.

Radial forces are thus set up in the particles that affect it exactly as though it were enclosed in a thin elastic membrane. Anything that increases the area of the surface of contact between the two phases absorbs energy, or requires force, for force is energy per unit area. The chemist or physicist finds the latter terminology more useful; the engineer often prefers the former.

If confusion is to be avoided, the reader must clearly bear in mind that the surface tension of a given liquid is not a distinctive property of the liquid itself but of the liquid and its environment. A drop of mercury resting on

glass, let us say, has a surface tension at the mercury-glass interface and at the mercury-air interface, and there is also a surface tension for the glass-air interface. The resultant force at the line of contact of the three substances is such as to keep the mercury a coherent drop resting on the glass and not spreading.

Substitute gold for glass and the resultant force is such as to favor an increase in the area of contact of gold and mercury, and the latter spreads out in a thin film and wets the gold.

These phenomena are of interest in considering soldering, welding, and the flotation processes of mineral separation. When surface tension of a liquid is mentioned without further restriction, air is considered to be the other phase. Any other gas, or a vacuum, would not materially alter the result.

Surface tension is very sensitive to changes of composition, cleanliness of surface, and so on. The practical effect is that laboratory determinations under carefully controlled conditions might have small relation to production methods.

Some generalization of surface tension has been attempted. The best known is the rule of Eötvös-Ramsay and Shields. This rule says that

$$\sigma V^{2/3} = k(T_c - 6 - T). \quad (2)$$

Here σ is surface tension, V molar volume, T_c the critical temperature of the liquid, and T the existing temperature. As always, temperatures are on the absolute scale.

The constant k is found to be nearly the same (2.12) for many liquids if σ is in grams per centimeter, V in cubic centimeters per gram molecular weight, and temperature in Kelvin degrees. The reader who has by this time forgotten all about critical temperatures may go back to Chapter 2, Equation (3), and renew the subject.

Differentiation of Equation (2) yields the expression

$$\frac{d\sigma}{dT} = - \frac{k}{V^{2/3}}. \quad (3)$$

If k could be accepted as a universal constant, the rate of change of surface tension with temperature would furnish a measure of molar volume and hence of molecular weight of a liquid metal.

Liquids are known for which k in Equation (2) is apparently much less than 2.12. This is true, for instance, of the low melting metals Zn, Cd, Sn, Pb, and Bi, for all of which k comes out about 1.1 on the assumption of monatomic molecules. If the elements were triatomic, the value of k would come out fairly well.

Ascribing departures from the Eötvös-Ramsay and Shields rule to such polymerization is, however, not very safe, lacking other means of confirming the existence of liquid molecules or their magnitude.

From van der Waals' Equation (2), Chapter 2, it would appear that the molar volume of a liquid at constant pressure would be of the form

$$\alpha V^3 - \beta V^2 + \gamma V - \delta = RT,$$

that is, that the expression relating the volume of a given mass of liquid to temperature would involve the cube, square, and first power of that volume. Since the temperature range during which metals are liquid in foundry practice is not large, and the coefficient of expansion rather small, it is usually customary to consider the coefficient of volume expansion as constant; in other words, the volume varies in proportion to temperature and the coefficient of linear expansion (of a solid) as one-third the volume coefficient.

There is little information available for metals of high melting point that is of such precision as to justify any more complicated expression.

Metals decrease in volume on freezing. In the iron-carbon alloys the decrease is about 6%, but during the separation of graphite in the eutectic liquid about half of this is made up by the amount by which graphite plus solid solution exceeds in volume the cementite from which they were formed. A few metals expand.

The volume change of other metals is not far from three times the patternmaker's shrinkage allowance appropriate to these metals when cooling without restraint, for example, as thin straight rods. Actually the volume decrease is slightly smaller.

The specific heat of liquid metals is usually considered constant. The entire subject of heat content has been treated at length as a fundamental field of science in Chapter 4, and comment has also been made in Chapter 3 on Grüneisen's relation of electrical conductivity to temperature as there shown by Equation (1) and on the relation of specific heat to coefficient of expansion. These relations should be considered in connection with the Wiedemann-Franz Equation (2) in Chapter 13 and the Debye function Equation (1) of Chapter 4, respectively. A combination of these portions of the text contains about all the generalized discussion of the subject that can be given.

Possibly the reader will be able to approximate data he needs from other data by the use of some of these principles.

Hydraulics

The flow of water in pipes and channels has been of importance to engineers for several centuries. First, quite simple relationships were devised and then improved by the use of various corrections. To one who, like the writer, is not a specialist in the subject of hydraulics, there is conveyed an impression that equations are used including constants that are not constants at all but are related to the condition of the problem as the result of empirical direct experiment, somewhat as is the case in some of the

heat flow problems with which we have already concerned ourselves.

Practically all these experiments have been made on water, and of the remainder nearly all concerned themselves with various solutions (oil and so on), leaving but an infinitesimal field of knowledge about liquid metals, especially mercury. Under these circumstances there will be no profit in struggling for an exhaustive treatment of the flow of liquid metals, and a discussion based on the older and simpler principles may give the foundryman all the information he can apply.

There are two kinds of flow to be considered. One is a quiet, laminar or striated type in which the elements of liquid move along approximately parallel paths without disturbing each other. The other is the turbulent type in which these lines of flow weave in and out among each other. The flow lines of laminar flow may be likened to the hairs of a violin bow; those of turbulent flow, to the strands of a rope.

Aside from turbulence produced by impediment, quiet flow goes over into turbulent flow at a certain critical value of the Reynolds number, usually represented by R_c and defined for round channels by the equation

$$R_c = \frac{2r\omega\rho}{\eta}. \quad (4)$$

Here r is the radius of the pipe, ω (Greek omega) the linear velocity of flow, ρ (Greek rho) the density, and η (Greek eta) the liquid's viscosity. Turbulent flow begins at Reynolds number near 2000. It is dimensionless and has the same value so long as all the constants are derived from the same units of time, mass, and length.

Most of the primitive work was developed on the assumption of quiet flow, and the laws do not hold for turbulent flow. The simplest of these laws is that in a straight channel of considerable length the resistance to flow is directly

proportional to the length and the *wetted perimeter* and inversely proportional to the cross section of the stream. The wetted perimeter is the length of that portion of the circumference of the stream of liquid which is in contact with the confining channel.

The Chézy formula states that

$$\omega = k \sqrt{Rs}, \quad (5)$$

where ω is linear rate of flow, k is a constant, R is the hydraulic radius (that is, twice the cross-sectional area divided by the wetted perimeter), and s is the loss of head per unit length. The *head* is the pressure expressed in terms of the height of a column of the identical liquid. The constant k includes a number of subsidiary constants. Obviously R is the radius for circular pipes.

Written for circular passages running full, the Fanning formula for h , the loss of head due to friction, is

$$h = 2f \frac{l}{d} \frac{\omega^2}{2g}. \quad (6)$$

Here f is a coefficient of friction depending on the container's surface condition, l is the length of the channel, d is its diameter, g is the gravitational constant, and ω is the linear superficial velocity of flow. The expression $2/d$ in Equation (6) is the R of Equation (5), and h/l is the s of that formula. The $2f/2g$ of Equation (6) is taken care of in k of Equation (5).

We are still left without knowledge of the empirical coefficient of friction f . The value of f is itself a function of ω via the Reynolds number.

For turbulent flow the velocity is not constant across the entire channel. The relation of f to R_e has a discontinuity around $R_e = 1000$ or $R_e = 2000$, where turbulence begins.

The variation of velocity of turbulent flow across the diameter of a circular pipe has been the subject of much

study. In foundry practice there will, in general, be but little justification for great refinement and but little interest in the principles. Although improved methods give increased precision, it will suffice in this present connection to refer to the Prandtl-Nikuradse equation, which correlates the velocity at various distances from the surface with the maximum velocity that exists at the center. The formula states that

$$(\omega_m - \omega) \sqrt{\frac{\rho}{\tau_0}} = -2.5 \ln \frac{y}{r}, \quad (7)$$

where ω_m is the maximum velocity of flow, ω is the velocity of flow at distance y from the inner surface of a pipe of radius r , ρ is the density of the liquid, and τ_0 is the shearing stress at the wall of the tube. The expression $\sqrt{\tau_0/\rho}$ is called the friction velocity. The number 2.5 is the reciprocal of von Kármán's universal constant (0.4).

Wang improved the mathematical treatment and the fit of the equation by the use of a rather complex mathematical expression which perhaps subtracts from, rather than adds to, practical utility for our present purpose.

Equation (7) evidently cannot be extrapolated to the wall of the pipe ($y = 0$), for then $\omega_m - \omega$ would be infinite. This implies an infinite ω_m (at the axis of the pipe) and hence infinite values of ω at all other distances from the wall except 0. The explanation of this fallacy is that in a thin layer near the pipe turbulent flow does not exist and the equations are inapplicable.

The Hagen-Poiseuille law states that for laminar flow in a round tube of radius r and length l the volume V of liquid flowing out in time t will be

$$V = \frac{\eta r^4 t}{8\eta} \frac{\Delta p}{l}. \quad (8)$$

Here Δp , the change in pressure from one end of the tube to the other, is in dynes and η is in poises, the units throughout

being in the cgs absolute system. The curve showing the distribution of linear velocity against distance from the axis is a parabola.

Viscosity determines the rate at which (small) spherical particles will fall (or rise) through a liquid. This rate has been used as a means of measuring viscosity, but we shall find it useful in its reverse form for considering the velocity. Written in the form most convenient for that purpose, the velocity of descent (or more often for our purpose ascent, corresponding to negative velocities) v , according to Stokes's law, is as follows:

$$v = \frac{2}{9} \frac{r^2 g}{\eta} (\rho_1 - \rho). \quad (9)$$

Here ρ_1 is the density of the sphere, ρ is the density of the liquid through which the sphere moves, and the other letters have their familiar meanings. The rate of rise of slag particles of radius r in metal can be computed.

The velocity of flow of liquids through orifices remains for consideration. The simplest are thin plate orifices, that is, channels having no length. In the simplest case the velocity of a liquid flowing from such an orifice is that of a particle of the same liquid falling from a height equal to that of a column of the same liquid exerting the existing pressure at the orifice.

Liquids contract after flowing out of such an opening, and the volume delivered is less than the area of the opening times the velocity calculated by the $\sqrt{2gh}$ relation. The ratio is called the coefficient of efflux of the orifice.

Other types of orifices (short tubes, bell shapes, and so on) have coefficients appropriate to their form.

The laws of flow have been considered in greater detail than our knowledge of the properties of liquid metals merits. This has been done more as a matter of general information than as a basis for actual quantitative treatment of foundry problems. Such treatment would involve

consideration of the fact that usually the flowing stream is constantly evolving heat with accompanying change, particularly in η and the terms dependent on it.

Surface Tension and Penetration

Surface tension enters into the question of flow of liquids by setting up a limiting pressure below which the liquid cannot enter a channel of given size.

Surface Tension and Wetting

If σ_{1-2} represents the surface tension at the gas-liquid interface, σ_{2-3} at the liquid-solid interface, and σ_{1-3} at gas-solid interface, then the surface of a liquid drop resting on a solid surface meets the latter at an angle ϕ such that

$$\cos \phi = \frac{\sigma_{2-3} - \sigma_{1-3}}{\sigma_{1-2}}. \quad (10)$$

This contact angle can be fairly readily measured.

Incidentally, if $\sigma_{1-2} + \sigma_{2-3}$ is less than σ_{1-3} the liquid will flow out to an infinitely thin sheet.

Whenever the surface tension of a liquid σ (by implication σ_{1-2} of the preceding discussion) is such that

$$\sigma \cos \phi = \frac{pR}{2}, \quad (11)$$

where p is the intensity of pressure (force per unit area) measured in the same units as σ , and R is the hydraulic radius, then the liquid will not move forward. It can only advance if pR is greater.

Instead of the somewhat complex considerations in accordance with which the behavior of a molten metal can be explained, the foundryman contents himself with a so-called fluidity test. This consists of a long, slender casting, usually in the form of a spiral, into which the metal to be tested is poured at a constant head. As the metal flows along the spiral it becomes more and more viscous

and increases in surface tension until presently near the freezing point it can advance no further. The distance it has flowed along the channel is then considered a measure of fluidity.

Investigations as yet unpublished have been made by Rightmire and others that at least partially correlate the length of flow in such an experiment with the thermal and mechanical properties of the metal.

Gating and Feeding

A MOLD CONSISTS essentially of the following components: (1) a sprue or downgate through which the metal flows from the top of the mold to the level at which it enters the casting; (2) one or more runners that are horizontal passages through which the metal flows to gates or openings into the mold cavity proper, which has the shape of the desired casting; and (3) a feeder to furnish liquid metal to the casting while it freezes.

The purpose of the whole arrangement is to conduct metal at the desired rate into the mold, without admitting any slag or particles of mold material, and then to supply from the feeder the necessary amount of liquid to prevent shrinkage voids.

The effect of liquid metal on the material comprising runners and gates (and sometimes parts of the mold cavity near the gates) is different from that in the mold cavity and feeders. In the former parts of the equipment there is a continuous stream of metal which keeps on supplying heat to the walls and also there is sometimes rapid motion through the passage which tends to erode the walls. In the latter parts the metal is usually somewhat static;

the mold wall may be exposed to radiant heat before the cavity is filled, but thereafter a skin of solid metal forms almost instantly, protecting the mold surface from further deterioration.

It is generally desirable, somewhere in the inlet system, to provide a constriction so that the metal flows through a submerged orifice, there being some depth of metal over this orifice on the upstream side. All this acts as a skimmer to hold back floating slag and similar material. It is best that this constriction be as near the mold cavity itself as possible to prevent further pickup of dross, and the gate is usually relied upon for this purpose.

Gas Pressure in Molds

While the mold is being filled there exists within it a certain pressure, so related to the rate of filling that air (or mold gas) flows out through the permeable mold walls just fast enough to make room for the entering metal. Although a quantitative treatment is impossible, a study of what happens in terms of pressures will furnish useful guidance.

The level of metal in the downgate, or sprue, is kept constant by the ladle stream. This level is above the level of metal in the mold (or above the level of the gate if the mold is not yet full to the gate), and there is thus a pressure head of liquid metal on the gas content of the mold. If we could express the loss of head in the sprue, runner, and gate in terms of rate of flow (in units of volume per unit time), the sum of these losses of head would exactly equal the total head of metal less the head equivalent to the amount by which the pressure of the mold gas exceeds that of the atmosphere.

The volume of gas leaving the mold includes not only the volume of inflowing metal but the increment of volume due to a rise of temperature and to the vaporization of gas-forming mold constituents. Furthermore, the volume

of outflowing gas decreases as the gas cools in flowing through the sand and condenses moisture (with possible blocking up of sand voids). An integration of these losses of head, if it could be performed, would be equivalent to the pressure in the mold.

Unless a mold is vented through a pop-off, that is, a small riser from the highest point of the mold to the upper surface, plainly the faster one attempts to fill a mold, the higher a gas pressure will be built up within and the more are swells or strains likely to occur.

The speed at which a mold is to be filled will depend upon whether or not it is desirable to have uniformity of temperature throughout the mold and riser, initially. In order that a riser may function, it must supply metal easily to the part of the casting last to freeze. This means progressive freezing, beginning at points distant from the riser and advancing toward it. If the riser is on top of a casting and the latter is filled slowly, the lower parts will be relatively cold by the time the riser is filled, thus favoring the efficiency of the feeder. All this assumes that the metal enters near the top of the mold. Here slow pouring is desired.

On the other hand, if a casting is poured from the bottom, as through a horn gate, slow pouring forces the entering metal, which is hottest, to push its way through a cold layer or push the latter ahead of itself. A feeder at the top might then be too cold, or cold shuts might be produced on the surface.

Also, since both viscosity and surface tension decrease with rising temperature, pouring must be fast enough to deliver metal to any thin and distant section without undue cooling.

Many alloys are subject to interdendritic shrinkage on cold pouring. A quickly poured casting often has less steep thermal gradients within it during cooling than one poured slowly, thus minimizing cooling stresses, to be

discussed later. In fact, the elimination of tears or cracks implies relatively low gradients of temperature, and the elimination of feeding, high gradients. The two are thus incompatible to a considerable extent. Practical solutions of pouring time are found experimentally, even though a rigid mathematical treatment is far beyond our ability.

Removal of Slag

If it is desired to use any part of the runner system as a means of floating out slag or sand, then the rate of flow in that passage will preferably be such as to be equivalent to a Reynolds number of, say, less than 1000. Otherwise, as discussed in the preceding chapter, turbulent flow will occur, keeping the inclusions churned up in the metal. Also, the time that a given lot of metal remains in this portion of the runner must be such as to permit particles of the smallest size that would be harmful to rise from the bottom to the top of the passage. The time can be computed by Stokes's law, also discussed in the preceding chapter. Unfortunately, practical conditions commonly involve larger Reynolds numbers and hence less efficient separation.

These considerations will determine the proportions of runners. Since the gates are often relied upon to choke the flow of metal so as to keep the runners full in the interest of skimming of slag, the linear rate of flow in the gates is usually the highest anywhere in the system. In principle a gate could be treated as a nozzle and submerged after the metal rose high enough in the mold. This would require a knowledge of the coefficient of efflux for the particular form of gate used. In the total absence of such data there seems little point in attempting a more detailed discussion.

There is a limiting value to the velocity of flow of metal in sand molds that is set by the erosive or washing action of the metal stream. First, the sand mold dries and there

is a tendency for sand grains to wash off. As more and more metal passes through the runner or gate the sand wall gets hotter and may, under unfavorable circumstances, even begin to melt and be washed away as a liquid.

The reader will be disappointed, no doubt, in our inability to treat quantitatively the design of runners and gates. Perhaps it is not a vain hope that someone will read the preceding chapter and determine some of the numerous, presently unknown, numerical values that would be required for the solution of actual problems.

Proportions of Runners

One point seems to be almost completely overlooked by patternmakers and foundry superintendents. This is that the rate of flow, under a given head, through a runner depends not only upon the cross-sectional area of the runner but also upon the geometric form of that cross section and upon the runner's length. The quantitative relations are discussed in the preceding chapter.

A frequent occasion where this error is of importance is when a symmetrical casting is to be filled from two gates connected to a single downgate or sprue by two runners of unequal length. The patternmaker is prone to make the two runners of the same cross section in the apparent belief that then the two gates will take equal amounts of metal. Actually the wetted perimeter of the two runners should be in inverse proportion to their length. An understanding of the quantitative laws of fluid flow will at least help us to solve some such problems.

Also often overlooked by the "practical" man is the fact that a stream of liquid metal behaves like all matter and obeys Newton's laws that a body at rest will continue at rest and a body in motion will continue to move in a straight line unless acted upon by an external force.

Metal flowing in runners usually moves rapidly enough to have (in view of its rather high density) so great a momentum that it will not turn aside or even downward

under relatively slight gravitational forces. Thus it will tend to flow past rather than through gates so long as there is a passage through which it can move ahead. Entering a mold through a gate it will generally pass, jetlike, partially or completely across until it encounters a wall which deflects it. Thereafter, even when the gate is completely submerged, it will set up whirlpool-like turbulence.

The U. S. Naval Research Laboratory has made excellent moving pictures illustrating, though not explaining, this phenomenon.

The question of heat transfer from molten metal to mold is complicated even for simple shapes and is virtually insoluble by calculation for complex patterns.

The need for introducing latent heat of fusion into the problem and also for considering heat transfer by convection removes the problem even in its simpler embodiments from the possibility of attack by the well-understood methods.

Freezing Time

A simplification was proposed by Chvorinov, who presented argument and data in substantiation of the hypothesis that the time required for any casting to freeze is proportional to the square of the ratio of its volume to its area. It has been shown that the freezing time for a portion of an infinite slab and for a sphere, of equal areas, is not proportional to the square of their volumes. This proof rested upon heat-transfer studies made in the electrical analogue of heat conduction by methods available only in a few laboratories. In rebuttal to this attack it is only fair to say, however, that Chvorinov's hypothesis has led to some practically useful results.

Risers

The most useful is in the design of feeders or risers. Here one is not so much concerned with absolute as with

relative freezing times. A casting has attached to it, usually at a high point, a reservoir of metal that must be so proportioned that some liquid metal remains in it when the casting is frozen solid. Assuming that casting and feeder are filled rather quickly, so that the metal in both is at the same temperature, freezing begins by the formation of a solid shell.

As the casting and feeder cool further, this established shell contracts, but its liquid contents contract still more, being initially lighter and hotter than the shell. There is thus formed a void whose volume is represented by the contraction accompanying the cooling of the liquid center and the contraction accompanying the change of state from liquid to solid.

The feeder is so placed and proportioned that it supplies enough liquid to the freezing casting to make up for this contraction. It is necessary that the feeder be of such dimensions that this liquid is available as the casting solidifies, and also it is necessary that liquid can pass from feeder to casting either by gravity or by suction, as liquid is sucked into a pipette. In either case the formation of a solid shell around the feeder, sealing the liquid within from atmospheric pressure, must be avoided either by keeping the surface metal in the feeder open, as by the addition of thermite, or by other, mechanical, means. The commonest device is a porous core penetrating the solid layer.

Covering a fair range of shapes and sizes of castings and feeders, Caine described before the American Foundrymen's Association in 1948 certain, perhaps purely empirical, rules for steel, which can be best described in a series of equations.

Let V_c and A_c be the volume and exposed area of the casting and V_f and A_f those of the feeder. Then if

$$x = \frac{A_c/V_c}{A_f/V_f}, \quad (1)$$

and

$$y = \frac{V_f}{V_c}, \quad (2)$$

a feeder will just suffice if

$$(x - a)(y - b) = c. \quad (3)$$

The constant a depends on whether a feeder is artificially cooled more or less slowly than the casting. If the feeder and casting are initially at the same liquid temperature and freeze without outside interference, then $a = 1$. For steel castings in which exothermic compounds are added to the feeder it may drop to 0.8 or perhaps lower.

The constant b represents the change in volume accompanying freezing, which Caine believed to be 0.03 for steel. The constant c for steel is empirically observed to be of the order of 0.10 or 0.12. Perhaps b should include also an allowance for fluid contraction, in which case an appropriate change in c would also be required.

Let the reader note carefully that the use of Chvorinov's ratio of area to volume does not depend for its validity on the acceptance of that author's conclusion. Equation (3) is derived directly from the experiment and is as true as the observations are accurate, no matter what one thinks of the Chvorinov rule. The observations took the form of noting the soundness or unsoundness of a series of castings and feeders for which a plot of x versus y was made and a line drawn by inspection to separate sound castings from shrunk ones. Since there is always some interlacing of good and bad at the boundary, there is some uncertainty in regard to c .

There are also some practical restrictions. A feeder can be effective only a limited distance along a casting, for instance. There may be heat transfer from feeder to casting; or feeder may be so placed that flow does not take place from feeder to casting. Another restriction is best

given as an example. A vertical cylinder of constant diameter, which might be regarded as a cylindrical feeder on a cylindrical casting, will shrink (neglecting end cooling) clear to the bottom. To avoid this the cross section of the feeder must be greater than that of the casting, near the latter's junction with the feeder.

These conclusions say nothing regarding the proportions of feeders, but if there is any merit in Chvorinov's ideas, then a feeder should have the least possible area per unit volume.

This suggests spherical feeders with small mouths, or a little less efficiently but more conveniently, a cylindrical feeder whose height equals its diameter and which also has a small mouth. If the feeder is to open into the casting by its full cross section, then a cylinder whose height equals its radius is the most efficient form.

If one of these or some other form is chosen as standard, then, so long as all feeders are geometrically similar, it is possible to set for A_f and V_f in Equations (1) and (2) their values in terms of one dimension, for example the radius, and get an equation in terms of the fourth power of r that can be solved graphically.

Note that Caine's relation is in terms of the *exposed* casting surface, which for fully connected feeders is πr^2 less than the actual area of the casting. An equation of the sixth degree in r results, which can still be solved graphically.

Shrinkage Voids

A good deal has been done regarding the shape and position of shrinkage voids but only for very simple shapes such as ingots. For a vertical cylindrical casting losing heat only from the curved surface, Feild has derived the equation

$$\log g = a \log x + \log h - 2a \log r. \quad (4)$$

Here x is the radial co-ordinate, y is the axial or vertical co-ordinate of a point on the surface of the shrinkage void,

and h and r are the height and radius of the cylinder. The coefficient of contraction on freezing is a .

For a tapered ingot where r_1 and r_2 are the radii at the top and bottom, Feild calculates

$$\log y = \log h + \frac{2a \log (x/r_1)}{\sin \theta} - \frac{a(r_2 - r_1)}{2.3x} + \frac{ar_2}{2.3r_1} - \frac{a}{2.3} \quad (5)$$

Here $\tan \theta = h/(r_2 - r_1)$.

Note that the only change in Equation (5) produced according to whether r_1 and r_2 is the greater is in the sign of the second and third terms.

Equation (4) requires that x becomes zero only when $y = 0$, that is, when the shrinkage extends to the bottom of the ingot.

Equation (5), if r_2 is less than r_1 , produces a shrinkage cavity whose bottom (at the center) is horizontal and at a finite distance above the bottom of the mold, the exact values depending on the ingot dimensions.

How deeply a shrink will be buried in a casting depends in any given pattern mainly on the degree of superheat of the metal. A void begins to form, of course, at the top of the still fluid metal when the mean rate of contraction of the liquid center becomes greater than that of the solid shell. This is largely a matter of temperature gradient, which in turn is related to the temperature of the liquid when it first filled the mold. Very cold pouring buries the shrink deeply; hot pouring may even produce a settle or external depression instead of an internal shrink.

Chills

Another method of promoting directional solidification is by the use of chills. These are pieces of metal, usually steel or cast iron, placed in the mold in locations where quicker cooling of the casting is desired.

In principle the transfer of heat from molten metal to the chill follows the rules of heat transfer already discussed in various places in this volume. Correct prediction of the functioning of chills is made difficult by the need for considering latent heat of fusion and the fact that, as in all other freezing problems, the cooling metal consists of an outer solid layer and an inner liquid layer.

Furthermore, it is known, and has been illustrated by Paschkis, that a casting freezing against a chill separates therefrom quite early, leaving an intervening air space that practically limits heat transfer from casting to chill to radiation and introduces a complexity due to the limitation of heat transfer at the surface of contact.

The purpose of a chill is to remove a given amount of heat, in a given time, from a given surface. How fast heat can be transferred depends on the diffusivities of the cooling and heating substances and on the resistance to heat flow across the surface of contact, besides of course, on the dimensions.

How much heat a given chill can absorb depends on its mass and the permissible temperature rise. Since heat transfer under the conditions where a chill functions is in the unsteady state, there will be a temperature gradient in the chill perpendicular to the mold surface. This gradient depends, of course, on the surface temperature and on the thickness and diffusivity of the chill and determines the rate at which the chill absorbs heat. For a given chill and rate of heat input, temperature gradients for different times can be deduced, or if we have ground for knowing the surface temperature, such curves can be drawn.

Usually any such calculations amount to little more than systematic guesses because of the number of variables whose magnitudes have to be estimated.

It can be shown, however, that there is some thickness of chill whose back surface will have risen a negligible amount when the casting was frozen. This has been called

by some an *adequate chill* because increasing its thickness would not increase its chilling effect. The other limit is a very thin chill that acts much as a slab with an insulated rear face and reaches a nearly uniform temperature, about equal to the surface temperature of the casting when it is frozen. Such chills are highly inefficient from the viewpoint of rate of heat removal.

What is no more than a crude first approximation as to chill behavior can be set up as follows. The surface of any but the thickest casting is not likely to be very far below the melting point of the metal until all is frozen. It can then be taken at some arbitrarily estimated lower value. The chill's surface temperature can then be guessed at as some lower amount.

From the estimated surface temperatures of the chill the rate of heat absorption per unit area for an adequate chill can be calculated, assuming an infinite thickness of chill. This rate, of course, decreases with time. The difference in temperature between casting surface and chill surface can be checked to see if by radiation the requisite rate of transfer is possible by the Stefan-Boltzmann law. If not, a better guess as to temperature difference can be made.

Plotting rate of heat transfer against time and taking the area under this curve from time zero to any desired t gives the total heat absorbed. The time required for the total heat absorbed to equal the enthalpy change of the casting from its pouring temperature to the assumed constant surface temperature is an approximation of the time required for the casting to freeze under the influence of the chill alone.

Inspection of the temperature gradients in an adequate chill will show that the final mean temperature rise is but a small fraction, 10% or 20%, of the temperature rise of the surface.

When using chills it is of course necessary that their sur-

faces never reach the melting point or they will weld on. Internal chills, on the other hand, are small metal objects, nails for example, set so as to project into the mold cavity. They withdraw heat from their surroundings by heating from room temperature to above their melting point, at least at the surface. The latter is necessary to secure welding into place and desirable in order to use up heat.

Residual Stresses

If we are to feed castings at all we must have temperature gradients. Parts of the casting distant from the feeder must solidify first and so on in order toward the feeder. Consequently when all is solid the metal is at different temperatures at different localities. The finished casting is at room temperature so that some parts of the casting have contracted more than others after solidification has been completed.

Either there are residual elastic stresses or there has been plastic deformation at high temperature, permitting an equalization of dimension. In addition there may have been constraint on shrinkage by the mold structure. It is desirable to permit stress relief, actually strain relief, during cooling, by allowing time for an equalization of temperature throughout the casting at the lowest temperature where such relief is practicable. In the iron alloys this may be near 500°C .

It is a general principle that if a metal specimen is stretched at a temperature above the recrystallization temperature, that is, without the possibility of work hardening, then instead of there being a single stress-strain curve, or a unique value of load for a given elongation (stress to strain), there are as many such curves as there are rates of stretch, the load for a given strain increasing as the rate of stretch increases.

This principle is of great importance in a consideration of cracking or hot tearing. It means that while the

strength of metal at a given temperature may have a specific value, as it probably does, the amount of stretch the specimen can undergo, without exceeding its strength, depends on the rate of stretch. The net effect is that metal at a given temperature will withstand a specific *rate* of stretch, not *amount* of stretch.

Now if two connected parts of a casting that restrain each other cool at unequal rates, the slower-cooling (and therefore hotter) section will be stretched at a rate proportional to the difference in cooling rate. This assumes a constant coefficient of thermal expansion. A correction is necessary if this simplification is not admissible.

The rate of stretch so produced may readily be the equivalent of the stress required for fracture within the limit of time, and therefore of stretch corresponding to the temperature conditions.

Although no investigator has given us experimental data for use in an equation, this consideration makes it quite plain that the time-temperature gradients in different mutually restraining parts of a casting must not differ by more than certain specific amounts or the casting will tear. The discussion could be made intolerably complicated if complex systems of stress were introduced. As in so many places in this book, and especially in this chapter, one can point to principles and discuss in words the general character of what will occur, but is able to deal quantitatively at best with simple problems and at worst with none. The foundry engineer of the future must supply the present gaps in our knowledge.

Let the reader carefully note that to promote soundness of casting, involving progressive freezing, large temperature gradients are an advantage, but to avoid tears, cracks, and residual stresses, temperature gradients should be minimized. Such contradictions as these are the cause of the foundryman's worries, requiring the most careful compromises.

Residual stresses arise out of inequalities of temperature that exist when the casting has reached a temperature so low that plastic deformation can no longer go on.

If a rod of unit length is cooled from temperature θ (above room temperature) to room temperature, it will contract by $\alpha\theta$ when α is the coefficient of thermal expansion. If the contraction is prevented from taking place, the stress situation is the same as though a rod were stretched, within the same temperature range, by $\alpha\theta$. We assume throughout that we are working below the recrystallization temperature.

For stresses S below the elastic limit the elongation of a unit length is S/E , E being Young's modulus of elasticity, and we may write

$$\frac{S}{E} = \alpha\theta. \quad (6)$$

Near room temperature E for iron alloys might be taken as about 29,000,000 lb. The coefficient of thermal expansion of steel is of the order of 12×10^{-6} (per °C). Then

$$S = 12 \times 29 \times \theta = 348\theta, \quad (7)$$

if S is in psi and θ in centigrade degrees.

If the elastic limit of a steel may be taken as approximating the yield point, which for a 0.30% plain carbon steel might be around 40,000 psi, not allowing for the deleterious effect of the as-cast structure, then $40,000 = 348\theta$ or

$$\theta = 115^\circ\text{C (above room temperature)} = \text{about } 140^\circ\text{C}.$$

At this temperature the assumptions as to E , α , and yield point are probably not too bad. The calculation will show how enormous the stresses are which can be set up by such restraints. If we set S as 100,000 psi, Equation (7) would no longer be applicable, for we would be in the plastic flow range.

Assuming that a steel of that tensile strength had an

elongation of 24%, an assumption which may or may not be right, depending on composition, then

$$\begin{aligned}12 \times 10^{-6} \theta &= 0.24 \\ \theta &= 2 \times 10^4.\end{aligned}$$

Evidently θ is far above any possible temperature at which recrystallization might cease; it is even far above the melting point. None of the assumptions have merit any longer, but the calculation shows that such a metal must flow plastically, given time, to adapt itself to anything that can be imagined. Actually steel castings contract only about 2% from the freezing point to the solid state. For steel we may set, roughly,

$$\theta = 500^\circ\text{C (above room temperature)}$$

as a maximum if recrystallization is not to occur; then

$$\begin{aligned}\alpha\theta &= 12 \times 10^{-6} \times 500 \\ &= 0.006 = 0.6\%,\end{aligned}$$

which is somewhere near the maximum value of the strain that can be required of steel under the postulated conditions.

The stresses that can be set up in complex castings under complex cooling conditions are enormously difficult to predict qualitatively since stress-strain curves for a given material vary with temperature and at elevated temperature with strain rate. It is easy to imagine shapes in which plastic deformation is prevented by the existence of restraint in several directions at a point, in which case stress-strain curves appropriate to the prevention of flow would be required, which is something else again.

We have come perilously near having to consider the applied mechanics of plasticity, a subject whose complexity is too great and whose application to the foundry is too slight to justify the space that would be required for a reasonably complete exposition.

Centrifugal Casting

This chapter may be concluded with a very brief allusion to the effects of centrifugal casting. In the main, the only effect is to drive metal more positively into what would otherwise be shrinkage voids, since centrifugal forces greater than gravity are easily attainable. The *casting* may be rendered denser but not the *metal*, which still consists of the same elements arranged in the same lattice.

There may be an effect on grain size and on segregation. If a metal develops centers of crystallization throughout, these solid particles are heavier than the liquid and of lower alloy content; accordingly they are driven outward in the spinning mass. Crystallites may even be torn from the inner surface and serve as nuclei in their passage outward. Thus the outer surface will contain less alloy and will be a mass of fine grains like a snowdrift, while the inner metal will be enriched in alloy, being deprived of the diluting effect of the crystallites driven to the surface. The inner metal will have but few crystallization centers and will, therefore, be coarse grained as frozen.

Now a few words as to the forces set up in centrifugal casting.

It is a matter of simple mechanics that a particle of mass m , rotating with an angular velocity ω (in radians per second) at distance r from the axis, exerts an outward force

$$f = m\omega^2 r. \quad (8)$$

Consider now a particle in the free inside surface of a liquid whirling in a cylindrical container that rotates about its own vertical axis.

The particle is acted upon by a horizontal centrifugal force,

$$f_c = m\omega^2 r,$$

and by the vertical force of gravitation,

$$f_g = mg.$$

Remember that the weight of a body, that is, the force with which it and the earth attract each other, is the product of its mass by the gravitational constant.

We wish to know the direction, with respect to the horizontal, of the resultant of the two forces, an angle we shall call ϕ . Plainly

$$\tan \phi = \frac{mg}{m\omega^2 r} = \frac{g}{\omega^2 r}. \quad (9)$$

The direction is independent of the mass of the particle. Since a liquid surface must be at right angles to the forces acting on it, because it cannot resist shear, ϕ is also the angle the surface makes with the vertical.

Now if r and h represent the horizontal and vertical co-ordinates of a point in the surface of the liquid measured with reference to an appropriate origin situated in the axis of rotation, then

$$\frac{dr}{dh} = \tan \phi = \frac{g}{\omega^2 r}, \quad (10)$$

$$r dr = \frac{g}{\omega^2} dh,$$

$$\frac{1}{2} r^2 = \frac{g}{\omega^2} h + I,$$

and

$$r^2 = \frac{2g}{\omega^2} h + I, \quad (11)$$

where I is a constant of integration that determines the value of h when $r = 0$.

The liquid surface is thus a parabola with a vertical axis. It grows steeper and steeper the greater the value of r or of ω .

Consider next the outward pressure of a cylindrical mass of liquid spinning on its axis. Since liquids transmit pressure equally in all directions, the shape of the radial cross section is immaterial. We treat of a wedge-shaped piece of the spinning liquid like a thin cut of pie whose area

at the base, or outer surface, is unity. Again because of the equality of pressure in all directions the shape of this element at right angles to the axis does not enter the problem.

A thin cross section of this element, at right angles to the radius, of a thickness dr has a mass ρdr , where ρ is the liquid's density. From Equation (8), the centrifugal force it exerts when spinning at radius r with an angular velocity ω (in radians per unit time) is then $\rho\omega^2 Ar dr$. Since pressure is the ratio of force to area, the increment of pressure exerted by this thin element is

$$dp = \rho\omega^2 r dr. \quad (12)$$

If the internal diameter of the spinning mass is R_1 , then the pressure at radius R_2 (which may if desired be the external radius) is

$$\begin{aligned} p &= \int_{R_1}^{R_2} \rho\omega^2 r dr \\ &= \frac{\rho\omega^2}{2} (R_2^2 - R_1^2). \end{aligned} \quad (13)$$

It can readily be seen that these pressures can become quite large, necessitating substantial mold construction. Also such internal pressure, acting on a hot frozen shell of metal, may deform it plastically considerably, producing castings of larger radial dimension than would a motionless mold of the same size and construction.

If any hydrostatic pressure exists, caused by feeder height, it is to be added to the above. It constitutes the constant of integration which was omitted from Equation (13) and which the mathematical reader will have missed.

Centrifugal casting, spinning on a vertical axis, has limits as to the axial length that can be cast, because of the mechanical inconvenience of keeping a high cylinder steady. If it is planned to have an exposed inner surface of the liquid, the parabolic shape of that surface may also be objectionable. Pipe, gun barrels, and the like are cast

while rotating about an essentially horizontal axis. This introduces a complexity that is but seldom recognized.

If a horizontal cylinder, partly filled with liquid, is rotated slowly on its axis, the liquid will merely stay put with a practically horizontal surface and the shell will rotate around it. The cylindrical mixers and ladles of the steel industry are examples. At slightly higher speeds, as in Brackelsberg furnaces, the liquid may be carried in the direction of rotation and may assume a surface inclined to the horizontal. Let us consider what is necessary in order that the liquid may be thrown to the upper surface.

Any particle of mass m in the surface of a liquid, spinning with its container and held against the *upper* surface by centrifugal force, is acted on by two forces. The centrifugal force is as in Equation (8), $f_c = m\omega^2 r$, and acts radially with respect to the axis of rotation. The force of gravity is $f_g = mg$ and acts vertically downward. If the particle is to be held up at all when it reaches the top, it must be that

$$\begin{aligned} f_c &> f_g, \\ m\omega^2 r &> mg, \end{aligned}$$

and

$$\omega^2 r > g, \quad (14)$$

which sets a minimum limit to ω and/or r for the process to work at all.

Consider the particle to be situated at an angle ϕ from the vertical, measuring from the top. The centrifugal force then acts at angle ϕ from the vertical and has vertical or horizontal components. Then

$$f_{c_v} = m\omega^2 r \cos \phi,$$

and

$$f_{c_h} = m\omega^2 r \sin \phi.$$

In this connection a vertical force is positive when acting upward, since $\cos \phi$ is positive if $\phi < 90^\circ$.

The net vertical force acting on the particle is

$$f_{c_v} = f_g = m\omega^2 r \cos \phi - mg, \quad (15)$$

and the angle that the resultant of this vertical force and the gravitational attraction makes with the vertical is given by

$$\begin{aligned} \tan \theta &= \frac{m\omega^2 r \sin \phi}{m\omega^2 r \cos \phi - mg} \\ &= \frac{\omega^2 r \sin \phi}{\omega^2 r \cos \phi - g}. \end{aligned} \quad (16)$$

The liquid surface is at right angles to this direction. Changing now the meaning of θ to indicate the angle that the liquid makes with the vertical at a point ϕ away from the vertical, then

$$\begin{aligned} \tan \theta &= \frac{\omega^2 r \cos \phi - g}{\omega^2 r \sin \phi} \\ &= \cot \phi - \frac{g}{\omega^2 r \sin \phi}. \end{aligned} \quad (17)$$

If y and x are the vertical and horizontal co-ordinates of a point in the surface, this becomes

$$\begin{aligned} -\frac{dx}{dy} &= \frac{y}{x} - \frac{g}{\omega^2 x \sin \phi} \\ &= \frac{1}{x} \left(y - \frac{g}{\omega^2 \sin \phi} \right). \end{aligned} \quad (18)$$

The negative sign of dy/dx originates from a change in the direction of rotation corresponding to a positive angle.

The free surface is a cylinder, not concentric with the axis of rotation. A simple means of determining this excentricity (whose value could also be derived from the preceding equation) is the following consideration.

If R_1 and R_2 are the radii from the center of rotation to the surface at the top and bottom of the free surface, equating the pressures on unit area at the two positions and canceling out mass as a common factor gives

$$\omega^2 R_1 - g = \omega^2 R_2 + g,$$

whence

$$R_1 - R_2 = \frac{2g}{\omega^2}, \quad (19)$$

and the center of the free surface is one-half this value or g/ω^2 above the center of rotation.

As the cylinder turns, evidently the inner portion at the bottom flows backward, and this amount of liquid either adheres to the surface a little at a time as freezing takes place or is churned up into a loose mass of crystallites on freezing.

It will be desirable to minimize the thickness of this layer by increasing ω . Its value is independent of R .

An important aspect of centrifugal casting too often overlooked by practitioners of that art is the assumption that a liquid mass rotates as rapidly as the container. If the liquid were ideal in being unable to resist shear, that is, if its viscosity were zero, it would never begin to spin. It does so only by virtue of its viscosity. Any study of the velocity of a particle in a spinning liquid as a function of the radius of its path and of the time since it was put into the spinning container, or since the latter began to rotate, would be of considerable complexity and would have a relation to the form of the liquid mass.

A simple case is the acceleration of a thin, hollow cylinder of liquid whose thickness is small compared to its radius.

An analogous equation for the force required to turn a journal on a stationary bearing is

$$P = S\eta \frac{V}{\delta}, \quad (20)$$

where P is the force, S the (cylindrical) area of the bearing, η the viscosity, V the linear velocity of the turning journal, and δ the thickness of the oil film. Our problem is the same except that there is nothing but inertia to keep the hollow cylinder from turning, and it will accelerate under the well-known relation of force to mass and acceleration

($f = ma$). Velocity is then no longer a constant but is $V_0 - at$, that is, the initial velocity minus the product of acceleration and time of spinning. Conversely the velocity of the oil ring is $at = x$.

We can then say, for unit axial length of the ring,

$$S\eta \frac{V_0 - x}{\delta} = \delta S\rho a,$$

or

$$\eta \frac{V_0 - x}{\delta} = \delta\rho \frac{dx}{dt}.$$

Integrating and remembering that $x = 0$ when $t = 0$, we have

$$\ln \frac{V_0}{V_0 - x} = \frac{\eta}{\delta^2\rho} t. \quad (21)$$

It follows that the speed of the ring approaches that of the spinning container logarithmically with time, and for a given degree of equalization of speed the time decreases as the viscosity increases and increases as the density of the liquid or the square of its density increases. The velocities are linear tangential velocity and equal to ωr .

The calculation assumes that the ring is so thin that its velocity is uniform. In thicker bodies the acceleration in the foregoing formula is the mean acceleration of the ring, which is a function of radius. The recognition of this variable increases the complexity of the problem without great benefit in the present connection.

CHAPTER 25

Distribution of Flame in Furnaces

NOW WE COME BACK to a subject that the reader may think should have been treated in Chapter 13 when the heating of objects in furnaces was discussed. It seemed better, however, to leave it until some of the laws of fluid mechanics had been taken up, for the flow of hot gases in a furnace involves the same principles as the flow of liquids in a channel.

Liquids flow in open channels, enclosed at the sides and bottom and in contact at their upper surfaces with the lighter fluid, air, with which they do not mix except for the slight transfer of liquid to air because of vapor pressure.

Flow of Hot Gases

Hot gases flow between the sides and under the roof of furnaces and in contact with the heavier and colder air in which the furnace is immersed, under precisely the same laws.

The subject was discussed, in Russian, at least forty years ago by Groume-Grjmailo, and in an English translation *Flow of Gases in Furnaces* (John Wiley & Sons, 1923), but has not since been given the emphasis it deserves.

Just as a liquid flows by virtue of a head exerting pressure because the liquid is heavier than the surrounding air, so with the light fluid flowing over a heavier one there is a head driving the stream of fluid along because of the difference in density between a column of heavy and light (cold and hot) gas.

Consider as the simplest example a chimney of height h in which the (absolute) temperature is T_1 while the temperature of the surrounding air is T_2 . Consider for simplicity that the gas inside and outside the chimney is the same, and that ρ_2 is its density at temperature T_2 .

The density of hot gas in the chimney will be $T_2/T_1 \rho_2$, since density is inversely as the absolute temperature.

Unit area at the base of the chimney sustains from the inside a weight of hot gas equal to $T_2\rho_2h/T_1$, and an equal area outside the chimney at the level of the base sustains a weight ρ_2h . The pressure at the top of the chimney is atmospheric inside and out, and so is neglected. Therefore, the difference in pressure at the base of the chimney inside and out is

$$P = \left(1 - \frac{T_2}{T_1}\right) \rho_2 h. \quad (1)$$

This pressure contributes the head that drives the hot gases up the chimney.

The chimney problem is recited mainly as a simple introduction. Apply the same principle to a furnace chamber of height h . Suppose we make two holes in the side wall, at the top and bottom. If the total pressure inside the furnace at the level of the upper hole is that of the outside air, the pressure at the bottom hole is less inside than outside by the value shown in Equation (1), and cold air will flow in. The head H actuating this flow will be

$$H = \frac{P}{\rho_2} = \left(1 - \frac{T_2}{T_1}\right) h, \quad (2)$$

and the linear rate of flow inward through the orifice,

considered for simplicity as in a thin plate and without correction for coefficient of efflux, will be

$$\omega = \sqrt{2gH}, \quad (3)$$

where H has the value from Equation (2) and g is the gravitational constant.

If on the other hand we arrange things in such a way that the pressure at the lower hole is the same inside and out, so that no inward flow occurs, then there is a pressure at the upper hole, equal to P of Equation (1), causing hot gas to flow out. The head producing that flow will be

$$H = \left(\frac{T_1}{T_2} - 1 \right) h. \quad (4)$$

From this a linear velocity of flow can be calculated from Equation (5).

Actually, there is little interest in the calculation of these flow rates. The purpose is to emphasize that it is not possible to balance the pressure inside and outside a hot furnace at more than one level.

A furnace will not heat properly unless the hot gases touch the material to be heated. Thus in a reverberatory melting furnace the flame must fill the space between the furnace roof and the level of the bath. If it does not, there will be an inflow of cold air at doors or other openings, tending to cool the bath.

We are thus led to an interest in the depth to which flame will fill a furnace. For a furnace with a horizontal roof the linear velocity of flow ω (in *meters* per second) is related to the depth of flame h_t (in meters) by the equation, ascribed by Groume-Grjmailo to Yesmann:

$$h_t = A \sqrt[3]{Q^2/B^2 T}, \quad (5)$$

where T is the Kelvin temperature, Q the volume of flow in cubic meters per second, and B the width of the furnace in meters. The constant A depends somewhat upon the

width of the furnace and the value of h_t . Groume-Grjmailo's tables of A are nearly equivalent to the statement that

$$A = 3.68 - \frac{0.8h_t}{B}. \quad (6)$$

It is very often true in furnaces of this type that it is desired to hold flame longer in the furnace, for better heat transfer, than could be accomplished by the dimensions of Equation (5). Just as a stream may be dammed up to produce a pond, so may the roof of a furnace be depressed

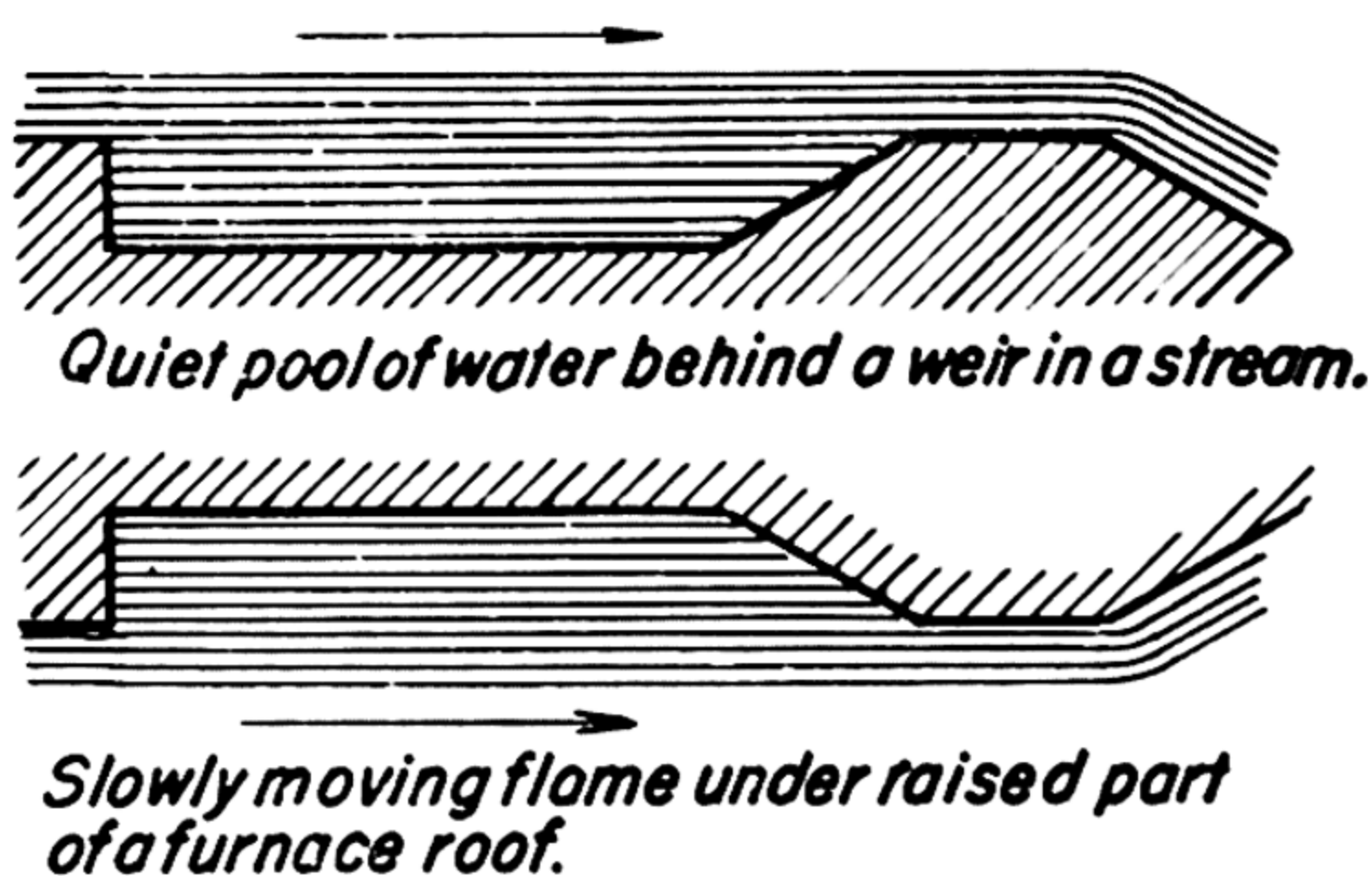


FIG. 25-1. Analogy of a Pond behind a Weir to a Furnace Roof Depressed at Rear.

at the rear bridge wall in accordance with Equation (5), making it possible to keep any desired depth of flame under the roof itself and thus producing any desired velocity of flow in the hearth.

As seen in Fig. 25-1 this condition amounts merely to raising a portion of a horizontal roof to produce any other form desired; Equation (5) will still apply for the depth of flame where it flows out under the roof at the rear.

A practical matter is that, since the flame will of course rise after passing under the lowest part of the roof, the rear bridge wall must touch the lower surface of the outflowing flame or cold air will enter between the top of the wall and the lower surface of the flame and cool the back of the bath.

If the bridge wall is higher than this it will choke the flow of flame.

The problem then becomes a question of the velocity of flow through an orifice. If the passage from bridge wall to stack is constructed so that the level of the flame is below the top of the bridge wall, this becomes a submerged orifice, and if Δd is the difference between the level of the flame upstream and downstream from the bridge wall, the linear velocity of flow will be approximately

$$\omega = 2g\Delta d. \quad (7)$$

This makes no correction for coefficient of efflux, an error that Groume-Grjmailo did not regard as important.

We come here to an important consideration regarding the height of the rear bridge wall above the liquid metal. If the furnace is carrying flame in contact with liquid metal we must exclude the layer of cold air that might lie on the metal until heated from above or by turbulence. Such a colder layer can escape only through an opening to the outside, below the level of the top of the bridge. Such openings exist to some extent in any structure inevitably and without special provision.

There will be no tendency to force this cold layer out, or to keep it from coming in, unless the height of the furnace above the metal bath and the bridge wall dimensions are so proportioned to the flow of flue gas that the furnace fills with flame. A useful expedient is to depress the roof beyond the bridge wall so nearly to the level of the bath that the flame must back up and fill the space above the metal.

In furnaces heating solid objects there is no problem, for the take-off can be at floor level. A little later we shall come to such furnaces again.

In many melting furnaces, open-hearth furnaces especially, the contact of hot gases with the bath is maintained by the jet-like action of the flame emerging from the burner.

The depth below the burner openings H to which a jet of flame leaving the burners with a linear velocity ω will descend if the direction of the burner makes an angle ϕ with the horizontal depends on the difference in temperature of the jet and the ambient gas, the composition of the two being assumed constant. If T is the absolute temperature of the furnace atmosphere and ΔT is the difference in temperature of the flame and furnace atmosphere, it follows from Yesmann's mathematics, quoted by Groume-Grjmailo, that

$$H = \frac{(\omega \sin \phi)^2}{2g} \frac{T}{\Delta T}. \quad (8)$$

Note that the jet *descends* in the furnace as the temperature of the latter's atmosphere approaches that of the jet of flame. Actually the value H is only approached, for the jet is retarded not only by the difference in density between it and its surroundings but also by friction (viscosity) with the surrounding gas.

Also, if the jet moves fast enough in relation to its cross-section to produce a Reynolds number sufficient to cause turbulent flow, it may merge with its surroundings.

In conclusion, we offer a few more words about heat-treating furnaces. Except in the case of continuous furnaces, these are, in general, much more nearly cubical than melting furnaces. Also, the rate of heat input per unit volume, and hence the volume of flame admitted in unit time, is relatively small.

If the flame is admitted near the bottom, and the vent is at the top, the hot gas will merely flow up along the near wall of the furnace, under the roof and out. It may not touch the charge at all, and the atmosphere surrounding the castings will heat but slowly, by conduction, and perhaps by fortuitous eddy currents.

If the outlet is at the bottom, the hot gases will rise, finally filling the furnace and flowing off at the bottom.

Consider, however, what happens when the circulation of gas is not uniform, but the hot gases chose by accident, or because of the character of the charge, a particular upward channel. This channel then becomes somewhat hotter than an adjacent downward passage, setting up, by the principles on which Equations (2), (3), and (4) are based, a still faster upward movement in the hot channel and downward in the cold.

The result is a further increase in temperature in the former in relation to the latter, with accompanying decrease in the uniformity of heating. If, however, the flame enters at the top and from the first follows some particular path, the heating of that path sets up an upward counter current of cooler gas and promotes the downward flow of gas elsewhere, thus equalizing the temperatures and making for uniform heating.

Similar principles apply to the heating of muffle furnaces. The flame should always enter above the muffle and flow downward over it to flues at the bottom. Attempts to distribute heat uniformly to the walls by other means are likely to encounter great difficulties.

Another example of these principles of circulation is found in radiant tube furnaces in which the heating elements are arranged vertically along the walls, outside the charge. The atmosphere reaches the tubes, is heated, flows upward to the top of the furnace and then downward through the interstices of the charge where it cools, flows to the bottom of the furnace, and starts its journey all over again.

Heat Exchangers

The principles just discussed are also applicable to the flow of cooling or heating gases through heat exchangers, whose purpose is to return the sensible heat of waste gases to the incoming air for combustion. In recuperators the hot flue gas and the cooler air flow in parallel channels, sepa-

rated by ceramic or, occasionally, metal walls. In regenerators the hot gases heat a checkerwork of brick on their way from furnace to stack. When the brick is sufficiently hot, the flue gases are diverted through a second similar checker, and the entering air is drawn through the hot checker from which it absorbs heat.

Evidently, in either case there are a multiplicity of parallel channels through which either gas can pass, and therefore it is important to arrange for the downward flow of the hot gas, or the upward flow of cold gas, in order to produce uniform heat flow and hence opportunity for uniform heat transfer in the several channels. It is fortunate that this requirement is consistent with the counterflow principle required for thermal efficiency, that is, that the hot and cold gases must pass through the exchanger in opposite directions to get any considerable benefit.

The need for this principle may be self evident. If it is not, consider the following example.

A furnace is operating with flue gas consisting of air whose oxygen content has been entirely converted to CO_2 . Its temperature is 2000°C above that of the atmosphere. Its sensible heat above atmosphere is entirely transmitted to the incoming air, so that the flue gas leaves the exchanger at atmospheric temperature and the air leaves it at 2000°C .

This situation represents complete efficiency so far as heat losses from the exchanger are concerned. The specific heats of oxygen and nitrogen at 2000°C are each 7.54, and that of CO_2 is 11.83, all in cal/g mol. The heat content of the flue gas as it leaves the furnace is then $2000 \times (4 \times 7.54 + 11.83) = 83,980$ cal/g mol of CO_2 . The heat content of the entering air is $2000 \times (5 \times 7.54) = 75,400$ cal/g mol of O_2 . One gram mol of O_2 produces one gram mol of CO_2 . Since a cold body cannot heat a hot one, the best possible efficiency would be $75,400 \div 83,980 = 90\%$ (about). The balance of the heat, if not

lost from the walls, escapes in the flue gas, contradicting the assumption that the flue gas escapes from the exchanger at atmospheric temperature.

Had the gases passed through the exchanger in the same direction, the best that could have been done would have been to have the flue gas go to the stack and the air to the burner at the same temperature. The specific heat of gases varies with temperature. If we call C_p that of oxygen and nitrogen and C_p' that of CO_2 , then the exit temperature T is such that

$$T(9C_p + C_p') = 83,980.$$

Taking suitable recognition of the specific heats, T becomes about 1100°C and the incoming air contains

$$1100 \times (5 \times 7.18) = 39,490 \text{ cal/g mol O}_2,$$

or about 47% of the heat in the flue gas as it leaves the furnace.

CHAPTER 26

Statistical Control of Processes

STATISTICS ARE OF INTEREST in a foundry or other industrial operation because they provide the only means of knowing how accurately any plant observation or record can be relied upon to represent a basic fact. We all know that no matter how hard we try, it is impossible to reproduce every time any given result, be it a matter of composition, mechanical properties, productivity, dimension, cost, or anything else. The methods of statistical mathematics permit reaching conclusions as to what degree of uniformity, in any such matter, can be expected under a given set of operating conditions. Also, one may get from them early warning when departures from the expected result are becoming so large or so frequent that some detectable source of error has crept into the process. Many very silly conclusions have been drawn and practices have been changed on the basis of differences of results that were not significant. A significant difference is a difference so unlikely to be produced by chance that that possibility may be disregarded.

Normal Distribution of a Property

The basis of most industrial statistics is the observation that the likelihood of occurrence of a given departure from the correct (usual, expected) value of some property has, for very many natural phenomena, a very definite relation to the magnitude of that departure. A number of such relations, applicable to particular circumstances, have been discovered, but the one most generally used and most frequently applicable is that discovered by Gauss over a century ago and often known by his name or by the name *normal distribution*.

This mathematical statement says that if many observations of a given constant x are made (for example, the carbon content of many heats of steel, all intended to be of the same composition, is determined), then the fraction of the total number of results falling between 0 and $\frac{x}{\sigma_x}$ from the average value, is

$$P = \frac{1}{\sqrt{2\pi}} \int_0^{x/\sigma_x} e^{-\frac{1}{2}\lambda^2} d\lambda. \quad (1)$$

Here P is the probability of occurrence, that is, as stated above, the fraction of the total falling between 0 and x , and hence the chance that any given value will fall within the prescribed range. The Greek letter lambda, λ , is a variable of integration that must include in its limiting value some evaluation of the scatter to be expected in values of x . This is the purpose of the term σ_x .

Standard Deviation, a Measure of Scatter

If one makes n observations of x , some coming out alike and some different, then as everyone knows, the average value, designated as \bar{x} in statistical notation, is

$$\bar{x} = \frac{\Sigma x}{n}; \quad (2)$$

that is, it is the sum of all n values of x divided by their total number n . The measure of the scatter of results is a calculated quantity called the *standard deviation* of x and designated by σ_x . It is defined by the expression

$$\sigma_x^2 = \frac{\Sigma(x - \bar{x})^2}{n - 1}. \quad (3)$$

That is to say, it is the square root of the sum of the squares of the n differences between each individual value of x and the mean value, divided by one less than the number of observations. Presently we shall come to certain easier forms of computation.

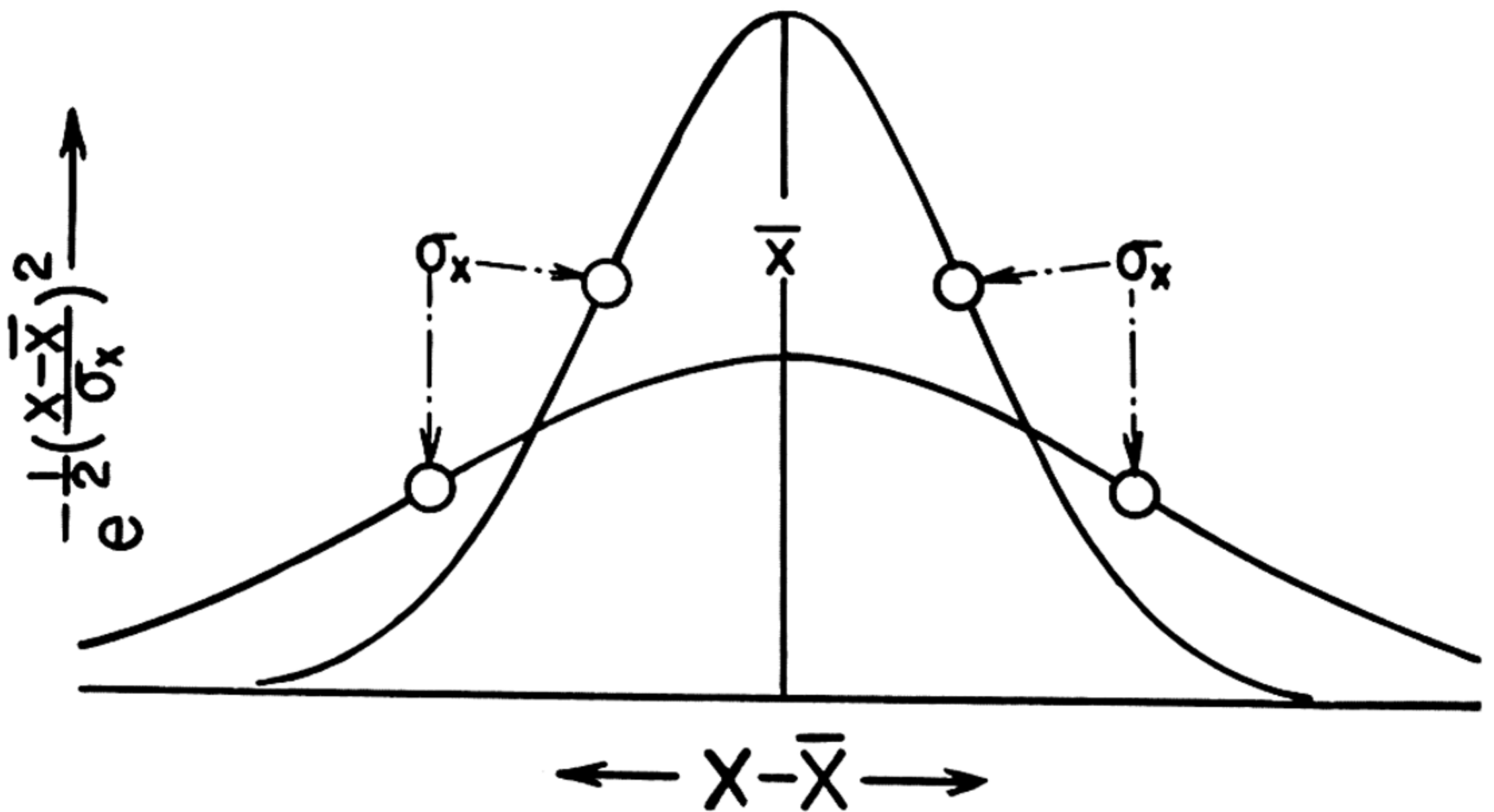


FIG. 26-1. Gauss's or Normal Distribution.

The expression after the integral sign in Equation (1) is shown graphically by the curves in Fig. 26-1. This figure represents the normal distribution of two lots of observations, called *populations* or *universes* in statistical terms, both having the same average or mean value \bar{x} but one having twice the standard deviation σ_x as the other. The two curves, which cannot be shown completely because they extend to infinity in each direction, both have the same area below them, this area being unity. The area under either curve between \bar{x} and any value of x/σ_x is

the same. In the present case, since σ_x of the flatter curve is twice that of the other, the area from \bar{x} to a given value of x on the flatter curve is equal to that of one-half that value of x on the steeper curve.

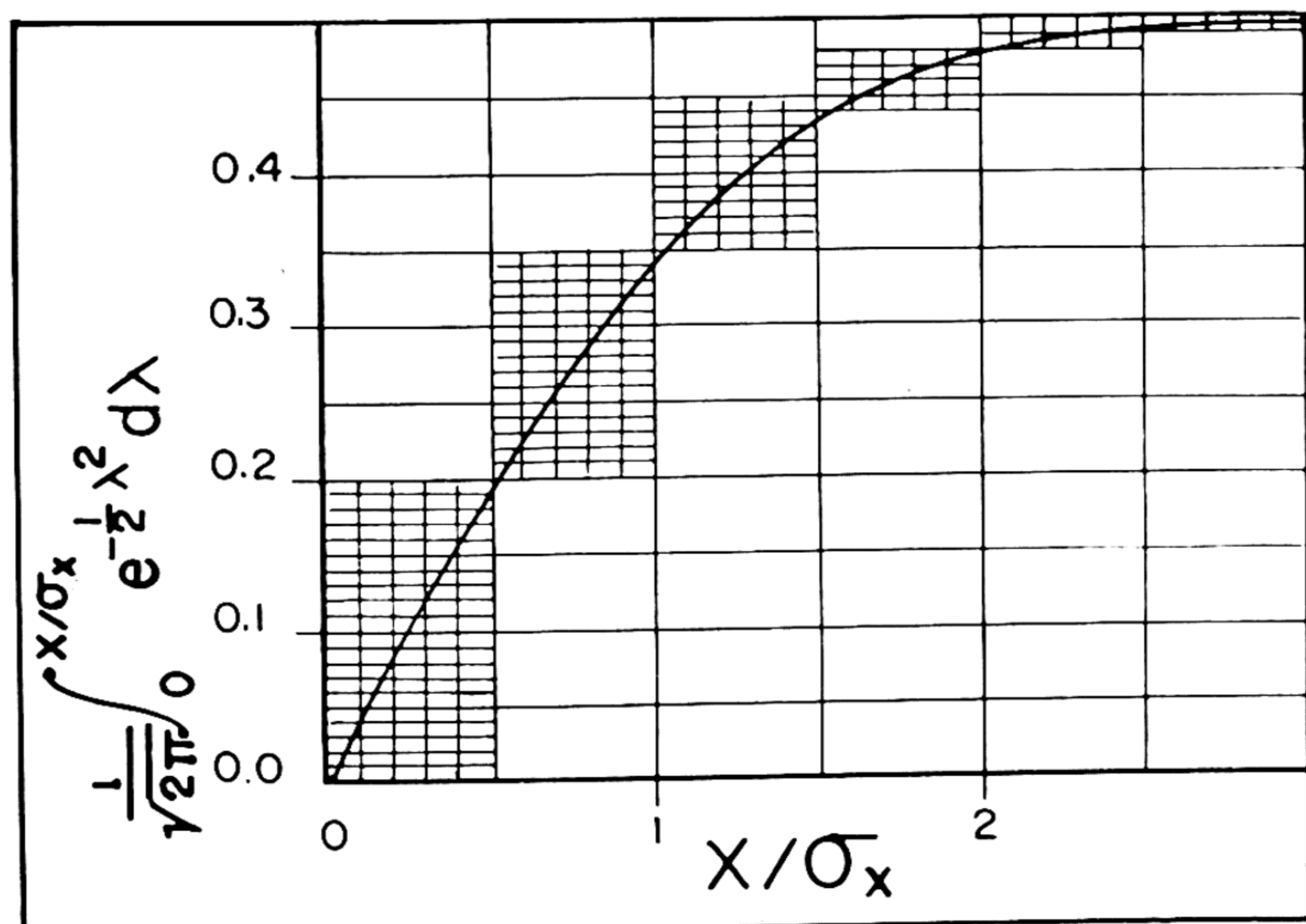


FIG. 26-2. Value of Probability Integral between $\lambda = 0$ and $\lambda = x/\sigma_x$.

The area between 0 and the upper limit of integration (x/σ_x for any specific case), that is, the value of P in Equation (1), can be found in the table of the probability integral to be found in most books of statistics and in many mathematical tables. The value of the integral is shown graphically in Fig. 26-2. The area from 0 to $x = \sigma_x$, that is, to $x/\sigma_x = 1$, is 0.3413; that to $x = 2\sigma_x$ is about 0.488; and that to $x = 3\sigma_x$ is about 0.4985. An older term still often used by physicists and astronomers, though not so convenient for statisticians, is the *probable error* (P.E.). Numerically this is 0.675 times the standard deviation. If $x = 0.675\sigma_x$, then the value of P in Equation (1) is 0.25. Then there is an equal chance that an observa-

tion will be nearer to or farther away from \bar{x} than this value; hence this error may be considered the most probable.

Equation (3) requires a good deal of arithmetical work for large values of n and in such cases the expression

$$\sigma_x = \sqrt{\frac{\sum (x - \bar{x})^2}{n}} \equiv \sqrt{\frac{x^2}{n} - \bar{x}^2} \quad (4)$$

is often substituted. The two radicals are mathematically identical. Few of the data encountered in engineering observations are sufficiently correct in themselves, so that if n is greater than 8 or 10, as it almost always is, any correction of Equation (4) is justified. However, if the value of σ_x from Equation (4) is multiplied by $\sqrt{n/(n-1)}$ the value from Equation (3) would be reproduced.

Another, and less accurate, method of obtaining the value of σ_x from a very large number of data without having to square all the readings is based on the fact that—assuming that a normal or Gaussian distribution relation exists and that all the subgroups have the same value of \bar{x} —it is possible to compute the most probable range of the numerical difference between the largest and smallest values in a subgroup of a given size. This size of subgroup is conveniently taken as either 4 or 5. Then if we divide all the readings in a universe, arranged in chronological order, into groups of 4 and compute the mean value of the differences between the largest and smallest values in each group, we can draw a conclusion from the mean range \bar{R} as to the value of the σ_x that produced it. The quickest way to compute \bar{R} is from

$$\bar{R} = \frac{\sum x_{\max} - \sum x_{\min}}{n} \quad (5)$$

Here $\sum x_{\max}$ and $\sum x_{\min}$ are, respectively, the sums of the largest and smallest values of x in each group of 4 (or 5), and n is the number of such groups, not the number of observations. The method is neither useful nor necessary

if n is less than 8 or 10. For subgroups of 4 the standard deviation of the average value is

$$\sigma_{\bar{x}} = 0.243\bar{R}. \quad (6)$$

Probability of Errors Exceeding a Given Magnitude

Having a value of \bar{x} and of σ_x for a given universe, we are now able to tell exactly how likely any given operation is to yield values falling more than a particular amount from the average. For example, if we know that the mean value of carbon in a steel made for a given purpose is 0.25% and its standard deviation is 0.02%, then we can say that 31.73% of the results ($1 - 68.26$) will be more than 0.02% away from 0.25%, that is, will be less than 0.23% or greater than 0.27%. About 5% of the values will be lower than 0.21% or higher than 0.29%, and practically none (actually 0.3%) will not fall within 0.06% of the average, that is, will be either below 0.19% or over 0.31%. Thus we have learned how to find out how accurate our knowledge is as to what the next carbon content will be; that is, what the chance is that it will be below some set value or above another.

This is the confusing point to those unfamiliar with statistics. They are familiar with mathematics that end in a definite conclusion regarding the precise numerical value of something. Statistics recognize that all observations, or other operations, are subject to error and end with a definite conclusion as to the most probable result coupled with an equally definite conclusion as to the chances that a given observation will be more (or less) than a specific amount away from this probable value.

Before proceeding further, the reader should be cautioned that many of the assumptions made so far and to be made later may not be completely justified. All distributions are not normal, the value of \bar{x} is not the same in all subgroups, and so on. The procedures of applied statistics

are in places not rigidly justifiable but represent practices that, as the result of long experience, are applicable in the evaluation of operating results. Readers *thoroughly* trained in statistics do not need this chapter; those new in science will make fewer mistakes by applying the methods here given than if they attempt to improve them.

Significant Differences

Knowing the scatter of values of x about an average, we are led to inquire into the scatter $\sigma_{\bar{x}}$ of a multiplicity of such averages obtained from various subgroups obtained from a given universe. It is found that

$$\sigma_{\bar{x}_n} = \frac{\sigma_x}{\sqrt{n}}. \quad (7)$$

That is, the standard deviation of the average of n values of x is the standard deviation of x divided by the square root of n .

This is but a step in determining whether two groups of results can be from a single universe. The practical importance of this question will be at once apparent. Suppose, for example, we desire to know whether or not steel of a given composition made in the electric and open-hearth furnaces is alike in reduction of area; it is an obvious approach to compute the average reduction of area for each of two considerable groups of steel of nearly uniform composition and compare the results. Unfortunately, the result of such a comparison is entirely inconclusive until it is known whether the observed difference could be the result of chance alone.

Standard Error of a Sum or Difference

It is one of the results of the study of propagation of error that the standard error of the sum or difference of two quantities can be calculated by the equation

$$S_{\Delta x} = \sqrt{\sigma^2 x_1 + \sigma^2 x_2}. \quad (8)$$

The standard error of the difference (or sum) of two values of x , $S_{\Delta x}$, is numerically equal to the square root of the sum of the squares of their respective standard deviations. The x of the equation can just as well be an average value as a single one when the x 's of the equation become \bar{x} 's.

Returning to our problem: If the two kinds of steel are interchangeable, then but for chance variations in sampling, the two average values would be equal, and their difference

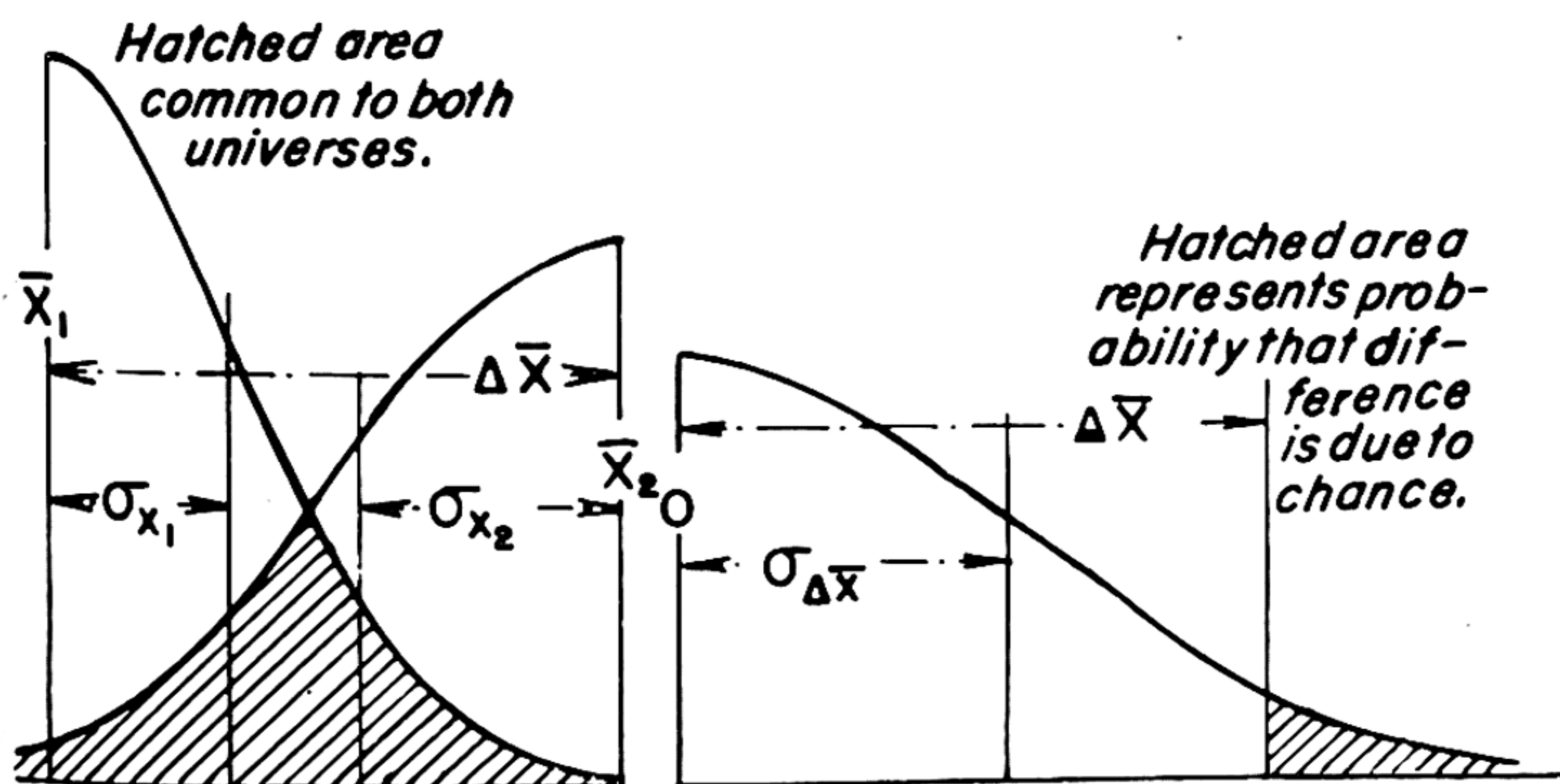


FIG. 26-3. Significance of Differences of Two Averages.

$\Delta \bar{x}$ would be zero but for the operations of chance. We must then determine whether an observed value of $\Delta \bar{x}$ could have originated from a single universe by comparing $\Delta \bar{x}$ with $S_{\Delta \bar{x}}$ as computed from Equation (8). Early in this chapter we learned that it is so unlikely that a given quantity will depart by over 3σ from its real value by chance alone (0.3%) that the possibility might well be disregarded. Therefore if $\Delta \bar{x}$ is greater than $3S_{\Delta \bar{x}}$ the two kinds of steel are not identical in reduction of area. Fig. 26-3 exemplifies these principles in graphic form.

The reverse, however, is not true. If $\Delta \bar{x}$ is less there is still some chance that the two universes (here two types of steel) are different. If $\Delta \bar{x}/S_{\Delta \bar{x}}$ is less than 0.675 it is

not so likely that the two universes are different as that they are alike, and as the ratio of $\Delta\bar{x}$ to $S_{\Delta\bar{x}}$ grows less and less, the likelihood of a real difference grows less and less, but we cannot reach certainty of identity, for any real difference up to $3S_{\Delta\bar{x}}$ could exist and by chance $\Delta\bar{x}$ could be zero. It is one of the advantages of statistical analysis that we are kept reminded of the possible extent of our ignorance and are led to consider whether our knowledge suffices to substantiate a given conclusion.

For example, if we were to consider the distribution of $\Delta\bar{x}$ about its mean value, we might perhaps find that $\Delta\bar{x} + 3S_{\Delta\bar{x}}$ would be small enough to be without engineering significance. This would mean that whether the steels were identical or not absolutely so, they would be identical from the viewpoint of use. The problem sometimes takes the form of wishing to determine whether a given change of practice (desirable for other, perhaps economic, reasons), can be adopted without danger of deterioration of some property of importance. In that case the average of the important property obtained by using the proposed procedure must exceed that obtained under the old procedure by more than three times the standard error of the difference. For some purposes of lesser importance such great certainty may not be required, and twice the standard error may be selected as a *fiduciary limit*, that is, test of satisfactory result. It all simmers down to how certain one has to be that his conclusions are correct. Invariably, however, it is found that those who go by horse sense accept conclusions as justified that statistics demonstrate to be acceptable only at considerable risk.

Correlation

In determining whether some variation of practice will affect the quality of a product, the statistic known as the *correlation coefficient* and represented by the letter r is most useful. Thus one might have a lot of cast irons

varying in carbon content and in castability as measured by the fluidity spiral and might wish to know the relation between the two properties. The correlation coefficient determines what fraction of the scatter in fluidities is due to scatter in carbon content. The value of r , the correlation coefficient of the properties x and y , is given by

$$r_{xy} = \frac{\overline{xy} - \bar{x}\bar{y}}{\sigma_x\sigma_y}. \quad (9)$$

Note that \overline{xy} is the mean value of the product of corresponding values of x and y , and $\bar{x}\bar{y}$ is the product of the mean values of x and y .

This fraction always has a value between $+1$ and -1 . If the value is $+1$ there is perfect positive correlation, that is, there is only one value of the dependent variable or effect, fluidity, for each value of the independent variable or cause and fluidity increases with carbon content and is unaffected by any other existing variable. A coefficient of -1 has the same meaning except that the effect decreases as the cause increases. A zero coefficient indicates no relation between the two variables, and the scatters are totally unrelated.

The correlation coefficient has a standard deviation

$$\sigma_r = \frac{1 - r^2}{\sqrt{n - 2}} \quad (10)$$

with which it must be compared to determine the likelihood that it is not due to chance alone.

A high correlation is necessary to prove that two things are related as cause and effect but it is not sufficient, for spurious correlations are quite common. Frequently the reason is that both variables are effects of a third one. An oft-quoted example is a certain investigation showing a close correlation between the salaries of school teachers and the arrests for drunkenness in the same community. Highly paid teachers did not contribute to drunkenness as

might be rashly concluded. When teachers' salaries are high, all earnings are high and more people can pay for enough liquor to attract the attention of the police.

Regression Coefficients

If a considerable degree of correlation is observed, one may wish to find out how much the effect, fluidity, will change for a given change in the cause, carbon content. To do so one determines the *regression coefficient* of the dependent variable fluidity on the independent variable carbon. This coefficient is commonly called b and

$$b = r \frac{\sigma_x}{\sigma_y}, \quad (11)$$

where x is the length of the fluidity spiral and y is the carbon content. The relation of x and y is then given by

$$x - \bar{x} = b(y - \bar{y}),$$

or

$$x = by + (\bar{x} - b\bar{y}). \quad (12)$$

One may wish to compare two processes with respect to their precision of control, preferring that which produces the least scatter of results. In the first problem suggested in this chapter as to electric and open-hearth melting, we may find that σ_x (x = carbon concentration) is different in the two universes. Are such differences real or due to chance? A standard deviation has itself a degree of uncertainty measured by its standard deviation which is

$$\sigma_{\sigma_x} = \frac{\sigma_x}{\sqrt{2n}}. \quad (13)$$

We can then compare $\Delta\sigma_x$, the difference of the two standard deviations, with the standard deviation of that difference as computed from Equation (13), just as Equation (8) was computed from Equation (7), and so on. If the standard deviation is derived through Equation (5), then the difference in scatter is reflected in a difference in

mean range. In a controlled system no single range can exceed $2.28\bar{R}$.

The most fruitful application of statistics in industry is in the control of quality of the product. Here quality can mean almost any measurable attribute, cost, rate of production, dimension, mechanical property, composition, inventory, business volume, and so on. Credit for this development is largely due to Shewhart of the Bell Telephone Laboratories. Statistical quality control has been taken up, often as the result of wartime experience, by many organizations.

The fundamental philosophy of statistical quality control is that if an operation is kept controlled in the sense that the results are normally distributed, and if the mean value and standard deviation of an attribute is known, then (1) it can be said with certainty that no result will fall below a certain known minimum, and (2) if any result falls outside the control limits, $\bar{x} \pm 3\sigma_x$, then an assignable cause of error exists; that is, something definite has happened that modifies the result of the operation.

Quality Control Charts

The practical application of statistical quality control, although it rests mainly on demonstrable mathematics, is to some extent an art and not a science. Few actual operating conditions conform so accurately to the basic mathematical assumptions as to justify rigid quantitative treatment, and certain compromises of technique are made necessary. Also there is the economic aspect of not going to the point of diminishing return for the statistical effort. The art is, however, somewhat complex and changes therein should not be lightly made by those not thoroughly versed in how to find out if they are desirable. Here there is no middle ground between proceeding according to authority or embarking upon a quite laborious study of mathematical principle and fact.

Certain assumptions are adopted by competent practitioners of the art of statistical quality control. It has already been said that the average of several values of an attribute is more likely to be normally distributed than the individual values; therefore one deals with averages of small groups instead of with single values. The smaller the group the quicker the warning, if an error creeps in, but the less justifiable the assumption that the distribution is normal. Experience has shown that taking groups of 4 successive values is a useful compromise, although 5 are sometimes used. Also, experience has shown that a transient cause of error that persisted only for a single observation cannot usually be traced, and warning as to its existence is not very useful. Also it is thought to be a sufficient test of normal distribution that no value fall more than 3σ from the mean (actually 3 in 1000 would be permissible), and on the other hand there could be an abnormal distribution without violating this test. Again experience has shown that sufficiently useful results can be had without the labor and delay involved in more elaborate tests of distribution. Indeed, such tests might actually be harmful as postponing action too long after a process gets out of control. In the interest of economy of effort, the range procedure is always used to determine the standard deviation, instead of the more accurate methods of computation.

The purpose of making a quality control study is to call immediate attention to a process that is yielding results that depart further from the desired value or scatter more than is consistent with the intent. The first step is, of course, to determine what is wanted and can be attained. Perhaps this is determined by a customer's specification. If he requires a steel whose carbon content is between 0.25% and 0.35%, obviously the desired mean value is 0.30%, and the grand average of many values should be exactly $\bar{x} = 30$. Also, plainly 3σ cannot be greater than 0.05;

that is, σ cannot be greater than 0.0167. If the melting process cannot be operated at so low a standard deviation, the specification cannot be met until the process is improved. An alternative, of course, is the segregation of each heat and the rejection of those outside the specified range, a proceeding generally prohibitive economically.

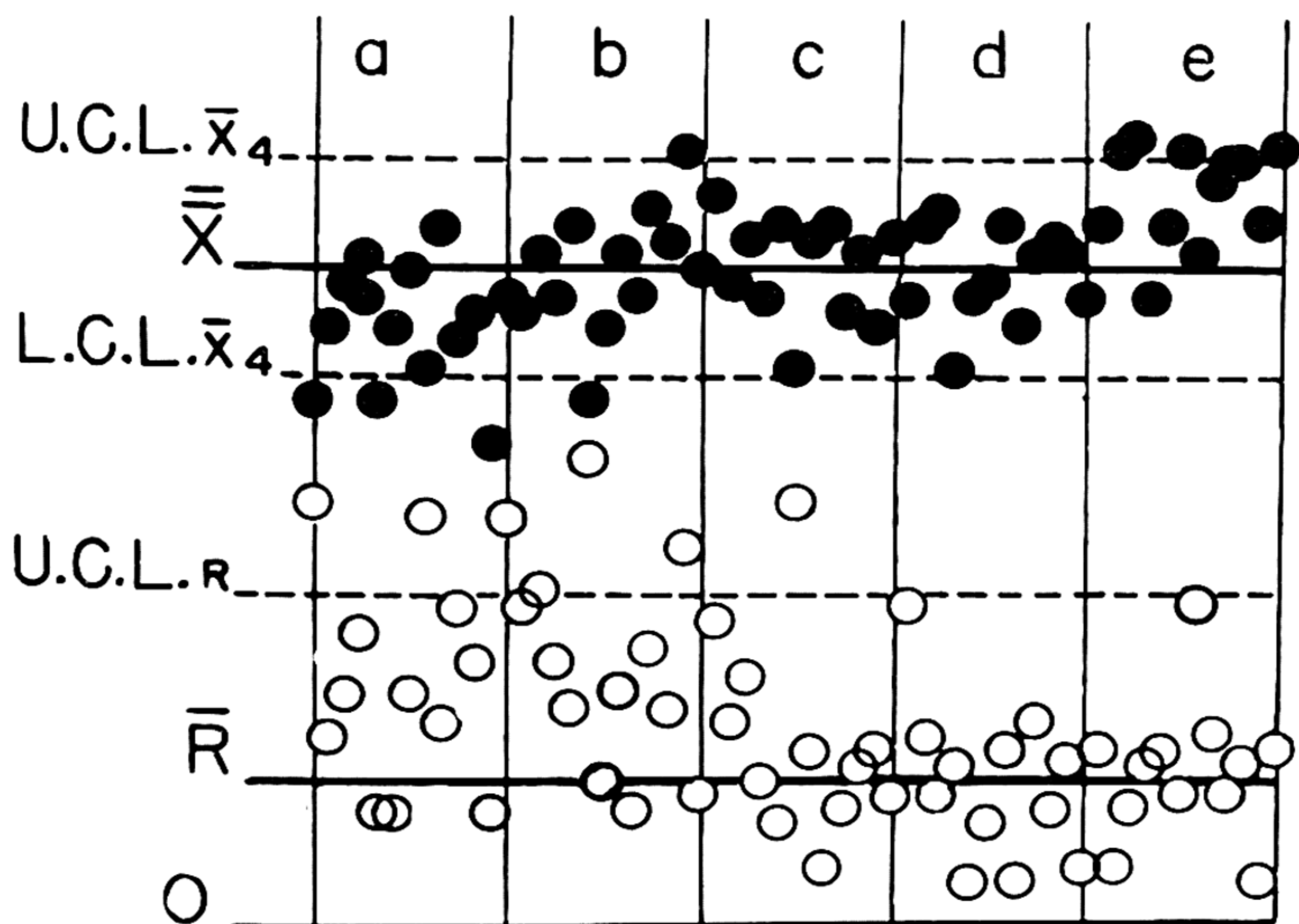


FIG. 26-4. Quality Control Chart.

Having determined the required σ , one may compute from $(2.28\bar{R})$ the mean range \bar{R} from Equation (6) and the upper limit of range consistent with the requirements. In the example chosen the numerical values are 0.07% and 0.16%.

When the choice is not dictated by specifications, it is determined by study of an extended period of past satisfactory operation. The essential in any case is to determine what mean value satisfies the requirements and what

degree of scatter, measured by standard deviation and resulting in a range of values, is attainable and sufficient to avoid the occurrence of substandard conditions. These facts being established, the next step is to proceed with the construction of a quality control chart as shown in Fig. 26-4.

First, one draws a line horizontally across the diagram at the desired mean value \bar{x} and two lines parallel to it and $3\sigma_x$ above and below it. These are called upper and lower control limits and no value of the average of four successive values \bar{x} may fall outside this band. If even one point does so, the system is out of control at that time. The purpose of the chart is to give notice of the condition and prompt an immediate and exhaustive investigation of what operating condition has changed.

Lower on the chart a horizontal line for the mean range \bar{R} corresponding to the established value of σ is drawn, and an upper control limit is drawn at $2.28\bar{R}$. If even a single value of R falls above this, even though the values of \bar{x} are within the control limits, the process requires investigation, for a greater scatter has occurred than the original controlled operation could have produced if unchanged.

The chart being established has plotted on it the average \bar{x} of each successive group of four observations and the range R in the successive group. An imaginary series of values is shown in Fig. 26-4. Deliberately they were put in to exemplify a series of operating conditions. In period *a* the mean range is obviously above the required \bar{R} , the average of \bar{x} falls below the required value, and many single values are outside the control limits. The system is random and not under control.

Usually the first effort would be to bring the value of \bar{x} nearer the desired \bar{x} , and this has been done in period *b*. However, some points still fall out of the control band because the conditions regarding range are unimproved.

In period *c* the range has been adjusted to average pretty close to the desired mean range, although an occasional range is still beyond the upper control limit. In period *d* the system is under control. In period *e* it is still under control but not at the desired level. The range conditions are as set up, but the values of \bar{x} fall above the established $\bar{\bar{x}}$, although between upper and lower control limits, not shown in the figure, consistent with the established range and the abnormal mean value.

It is sometimes established that where a minimum (or maximum) value of an attribute is specified, such a value should also be drawn on the chart and no single value shall fall below such a minimum, even though the averages of four are all above. Also it is well to remember that the likelihood that *m* successive values will all be in the same side of \bar{x} is 2^{m-1} , and the chance that *m* values will each be higher (or lower) than its predecessor is the same. For *m* = 10 this means only one chance in 64 that the result is due to chance alone and not to a progressive change in the process. The chance that a numerical value will fall between 2σ and 3σ on a given side of \bar{x} is only 0.05. The chance that two successive values will so fall is 0.0025, and three successive ones, 0.000125. Need it be emphasized that the frequent occurrence of numerical values near the upper and lower control limits is evidence that control is being lost?

Quality control charts give no indication of the nature of an assignable cause when an operation goes out of control.

It is an operating matter to investigate the cause of lack of control. Sometimes correlation studies serve to determine what variables must be controlled, if the process as a whole is also to be controlled. It may happen that if many causes contribute to a result, the total operation will be under control statistically, even if each cause separately is not.

This chapter and this book may well be ended with the statement that an effort has been made to give to the foundry engineer information as to principles that may serve as guides to successful practice. It remains for him to make suitable applications as required if he is to benefit from a reading of these pages.

Supplementary Reading

THE TREATMENT OF all the subject matter of the preceding text has been made as concise as possible. Little attempt was made to establish the validity or the background of the treatment. Those desiring a more thorough understanding will find most of what they want in the following suggested reading list. This is not to be regarded as a documentation of each separate statement. It is arranged by chapters and the references are to publications which deal with the general subject matter of that chapter rather than with individual facts. Most of the references are to books. These always contain also information on subjects not included in the particular chapter. This is particularly true of the physical chemistry and thermodynamics texts distributed through the several chapters and in some cases referred to in more than one chapter. The references are either to fairly recent treatments of the several subjects, to publications which have become classics in their fields, or to original source material. Many of them will be found to contain further references permitting the student to go as far as he likes in his reading. References to elementary physics or chemistry texts were omitted as superfluous.

Chapter 1

"The Atom," anonymous. *Life*, page 68 (May 16, 1949).

"The Neutron, the Intermediate or Compound Nucleus, and the Atomic Bomb," by William Draper Harkins—*Science*, vol. 103, no. 2671, page 289 (March 8, 1946).

An Introduction to the Electron Theory of Metals, by G. V. Raynor, (British) Institute of Metals Monograph No. 4 (1947).

The Fundamental Concepts of Physics, by Paul R. Heyl, Williams and Wilkins (1926).

Space and Time in Contemporary Physics, by Moritz Schlick, Oxford University Press (1920). (Background material.)

Chapter 2

Treatise on Physical Chemistry, by Hugh S. Taylor, Van Nostrand (1924).

The Phase Rule and Its Applications, by Alexander Findlay, Longmans, Green (1918).

Chapter 3

The Physics of Metals, by W. Boas, Wiley, (1947).

Introduction to Chemical Physics by J. C. Slater, McGraw-Hill (1939).

The Structure of Crystals, by Ralph W. G. Wyckoff, Chemical Catalog (1931).

The Structure of Crystals (supplement to the preceding), by Ralph W. G. Wyckoff, Reinhold (1934).

The Modern Theory of Solids, by Frederick Seitz, McGraw-Hill (1940).

"Kompressibilität und Elektronen Volumen," by H. Koppe, *Zeit. Anorg. und Algem. Chemie*, vol. 24, page 131 (1941).

"Review of Certain Aspects of Metal Physics," by G. M. B. Douglas and R. W. Powell, *Journal of Iron and Steel Institute (British)*, vol. 162, page 289 (1949). Numerous references.

Chapter 4

Fundamentals of Physical Chemistry, by Arnold Eucken, Eric R. Jette, and Victor K. LaMer, McGraw-Hill (1925).

Chapter 5

Specific Heat of Gases, by J. R. Partington and W. G. Schilling, Van Nostrand (1924).

Physical Chemistry Texts referred to elsewhere.

"Vapor Pressure of Zinc and Cadmium over Their Silver Alloys," by G. E. Birchenall and C. H. Gheng, *Journal of Metals*, A.I.M.M.E., vol. 1, no. 7, page 425 (1949). References to other systems.

Chapter 6

Thermodynamics for Chemists, by Samuel Glasstone, Van Nostrand (1947).

Chapter 7

The Structure of Metals and Alloys, by William Hume-Rothery, Institute of Metals, London (1936).

Unknown Title, by Schroeder, *Zeit. Physik. Chem.* vol. 11, 449 (1893). See Arnold Eucken, Eric R. Jette, and Victor K. LaMer, page 219 (reference, Chapter 4).

Chapter 8

"Grains Phases and Interfaces," by C. S. Smith, *Trans. A.I.M.M.E.*, vol. 175, page 15 (1948).

Chapter 10

Fuels and Their Combustion, by Robert T. Haslam and Robert P. Russell, McGraw-Hill, (1926).

Chapter 11

Contributions to the Data on Theoretical Metallurgy, by K. K. Kelley, U. S. Bureau of Mines Bulletins Nos. 350 (1932); 371 (1934); 383 (1935); 393 (1936); 394 (1935) and 407 (1937).

"Thermodynamics of Substances and Interest in Iron and Steel Making: I-Oxides," by F. D. Richardson and J. H. E. Jesses, *Journal of Iron and Steel Institute (British)*, vol. 160, page 261 (1948).

Chapter 12

Thermodynamics, by Gilbert Lewis and Merle Randall, McGraw-Hill (1923).

Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards (1948).

Chapter 13

Heat Conduction, by L. R. Ingersoll, O. J. Zobel, and A. C. Ingersoll, McGraw-Hill (1948).

Flow of Heat in Metals, by J. B. Austin, American Society for Metals (1942).

Applied Mathematics in Chemical Engineering, by T. K. Sherwood and Charles E. Reed, McGraw-Hill (1939).

The Solution of Transient Heat Conduction Problems by Finite Differences, by G. A. Hawkins and J. T. Agnew, The Engineering Experiment Station, Purdue University, Research Bulletin No. 98 (March, 1947).

"The Numerical Solution of Heat-Conduction Problems," by H. W. Emmons, *Trans. A.S.M.E.*, vol. 65, No. 6, page 607 (1943).

Chapter 14

Industrial Electric Furnaces, by Victor Paschkis, Interscience (2 volumes) (1945) (1948).

Chapter 15

Pyrometric Practice, by Paul D. Foote, C. O. Fairchild, and T. R. Harrison, Technologic Paper No. 170, National Bureau of Standards (1921).

Chapter 16

Physical Chemistry of Metals, by Rudolph Schenck and R. S. Dean, Wiley (1919).

Chapter 17

The Physical Chemistry of Steel Making, by C. H. Herty, Jr., Mining and Metallurgical Advisory Board, Pittsburgh (1934).

The Manufacture of Electric Steel, by Frank T. Sisco, McGraw-Hill (1924).

Open Hearth Steel Making, by Earnshaw Cook, American Society for Metals (1937).

"Inclusions, Their Effect, Solubility and Control in Cast Steels," by C. E. Sims and G. A. Lillieqvist, *Trans. A.I.M.M.E.*, vol. 100, page 154 (1932).

Chapter 18

Texts in Physical Chemistry already listed.

Diffusion in and through Solids, by Richard M. Barrer, Macmillan (1941).

Chapter 19

Handbook of Cupola Operation, American Foundrymen's Association (1946).

"Economics of Cupola Operation," by F. K. Vial, *Trans. A.F.A.*, vol. 54, page 507 (1946).

Chapter 20

Principles of Phase Diagrams, by J. S. Marsh, Alloys of Iron Monographs, Engineering Foundation, McGraw-Hill (1935).

Alloys of Iron and Carbon, by Samuel Epstein, Alloys of Iron Monographs, Engineering Foundation, McGraw-Hill (1936).

"A Thermodynamic Study of the Iron-Carbon Diagram," by J. B. Austin, *Metals and Alloys*, vol. 4, page 49 (1933).

"A New Structural Diagram for Cast Iron," by H. Laplanch, *Metal Progress*, vol. 52, no. 6, page 991 (1947).

"Kinetics of Graphitization of White Cast Iron," by H. A. Schwartz, *Trans. A.S.M.*, vol. 30, page 1728 (1942).

"The Conversion of Solid Cementite into Iron and Graphite," by H. A. Schwartz, *Journal of Iron and Steel Institute (British)*, vol. 138, no. II, page 205 (1938).

"The Freezing of Cast Irons," by Alfred Boyles, *Trans. A.I.M.M.E.*, vol. 125, page 141 (1937).

"Graphite Formation in Gray Cast Iron," by H. Morrogh and M. J. Williams, *Foundry Trade Journal*, vol. 82, page 319 et seq. (1947).

"Theories of Gray Iron Inoculation," by H. W. Lowrie, Jr., *Trans. A. F. A.*, vol. 50, page 837 (1946).

"Producing Nodular Graphite with Magnesium," by C. K. Donoho, *American Foundryman*, vol. XV, no. 2, Page 30 (February, 1949).

Modern Metallurgy for Engineers, by F. T. Sisco, Pitman (1948).

Some Effects of Deoxidation Treatment on Graphitization of White Cast Iron, by Richard Heine. Reprint 49-8, A.F.S. (1949).

"Role of Centers of Graphitization in the Annealing of Malleable Iron," by S. A. Saltikov, *Metallurg.*, vol. 14, no. 8, pages 10-22 (1939). (In Russian; translated by Henry Bratcher, 1949.)

Chapter 21

"Hardenability Calculated from Chemical Composition," by M. A. Grossman, *Trans. A.I.M.M.E.*, vol. 150, page 227 (1942).

The Alloys of Iron and Silicon, by Earl S. Greiner, J. S. Marsh, and Bradley Stoughton, *Alloys of Iron Monographs*, Engineering Foundation, McGraw-Hill (1934).

"The Location of Elements in White Cast Iron," by H. A. Schwartz and James Hedberg, *Trans. A.S.M.*, vol. 40, page 223 (1948).

"Iron, Carbon and Sulphur," by Donald Levy, *Journal Iron and Steel Institute (British)*, vol. 77, page 33 (1908).

Chapter 22

Bonding Action of Clays in Green Sand Molds, by Ralph Grim and F. Leicester Cuthbert, Engineering Experiment Station Bulletin No. 357, University of Illinois (1945).

Bonding Action of Clays in Dry Sand Molds, by Ralph Grim and F. Leicester Cuthbert, Engineering Experiment Station Bulletin No. 362, University of Illinois (1946).

Diffusion in and through Solids, by Richard M. Barrer (listed in Chapter 18), Macmillan (1941).

"Effect of Grain Shape on the Behavior of Synthetic Core and Molding Sands," by W. J. Rees, *Ceramic Digest*, vol. 1, no. 6, page 212 (July, 1948).

Chapter 23

Fluid Mechanics for Hydraulic Engineers, by Hunter Rowse, McGraw-Hill (1938).

"Imaginary Contact Angles and the Jones-Ray Effect," by Albert Sprague Coolidge, *Journal of American Chemical Society*, vol. 71, page 2153 (1949).

"Measurement of Interfacial Tensions," by J. C. Fisher, *Trans. A.I.M.M.E.*, vol. 175, page 906 (1948).

"Fluidity Testing of Foundry Alloys," by K. L. Clark, *Trans. A.F.A.*, vol. 54, page 87 (1946).

"Theory of Surface Tension of Metals (Solids)," by A. E. Glauberman (Russian), *Journal of Physical Chemistry*, vol. 23, page 115 (Feb. 1949); Abstract 3A, 128, *Metals Review*, vol. XXII, no. 7, page 22 (July, 1949).

"Fundamental Characteristics of Casting Fluidity," by V. Kondic and H. J. Kozlowski, *Journal, Inst. of Metals*, vol. 75, page 665 (1949).

Leçons sur les Fluides Visqueux, by Henri Villat, Gauthier-Villars et Cie (Paris, 1943).

Chapter 24

The Metallurgy of Steel Castings, by Charles W. Briggs, McGraw-Hill (1946).

Solidification of Metals, by H. A. Schwartz, A.F.A. Publication No. 45-1 (1945).

"A Theoretical Approach to the Problem of Dimensioning Risers," by J. B. Caine, *Trans. A.F.S.*, vol. 56, page 492 (1948).

"Residual Stresses in Metals," by W. M. Baldwin, Jr., Washburg Lecture, A.S.T.M. (1949). (To be published.)

"Stress Relief Heat Treatment of Alloy Cast Iron," by M. M. Hallet and P. D. Wing, *Foundry Trade Journal*, vol. 87, no. 1719, page 177 (Aug. 11, 1949).

"Two Problems of Thermal Stress in the Infinite Solid," by N. O. Myklestad, *Journal of Applied Mechanics*, A.S.M.E. page A-137 (1942).

Chapter 25

The Flow of Gases in Furnaces, by W. E. Groume-Grjmailo, Wiley (1923).

Open-hearth Furnace Models: Part I—"Flow Patterns in Ducts," by J. H. Chesters and A. R. Phillips, *Journal of Iron and Steel Institute* (British), vol. 162, part 4, page 384 (Aug. 1949); Part II—"Flow Visualization and Photography," by R. S. Howes and A. R. Phillips, *ibid.*, page 392; Part III—"Flow Patterns in Model Furnaces," by I. M. D. Halliday and A. R. Phillips, *ibid.*, page 401.

Chapter 26

Outline of Statistical Methods, by Herbert Arkin and Raymond Colton, Barnes and Noble, (4th ed., 1939).

Methods of Correlation Analysis, by Mordecai Ezekiel, Wiley (1941).

Economic Control of Quality of a Manufactured Product, by W. A. Shewhart, Van Nostrand (1931).

Control Chart Method of Controlling Quality during Production, anonymous, American Standards Association (1942).

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